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Matter, Electricity, Energy

The Principles of Modern Atomistics and Experimental Results of Atomic Investigation

By

WALTER GERLACH
o. ö. Professor, University of Tübingen

TRANSLATED FROM THE SECOND GERMAN EDITION
BY

FRANCIS J. FUCHS, PH.D.
St. John's College, Brooklyn, N. Y.

NEW YORK
D. VAN NOSTRAND COMPANY, INC.
EIGHT WARREN STREET
1928

PREFACE TO FIRST GERMAN EDITION

The present volume differs essentially from other books on this subject in the manner in which the subject is treated. The preference for this difference in treatment is feasible because, in the first place, the development of general atomistics, its extension to a large number of physical problems of the most divers domains, viz.: to inorganic chemistry—and by way of experiment—to organic chemistry, to mineralogy, to astronomy and finally its direct application in technique, have progressed so stupendously during the last ten years that the mere presentation of this development and its results, as illustrated by data selected from the original researches, would require a treatise much more extensive than is available within the limits of these pages. Furthermore, such a treatise seems not only aimless, but also unnecessary, inasmuch as the more important phases find adequate discussion in monographs especially devoted to them. Secondly, in the author's opinion, this form of treatment is justified because of the utter lack of any exposition of the present status of atomistics intended to appeal, not so much to the trained physicist as to the natural scientist and to the philosopher, whose interest in the deeper knowledge of nature is assumed, but—unfortunate to state—which must first be aroused. Consequently this treatise should appeal more directly to the chemist, to the mineralogist, to the technical physicist, to the engineer, in short, to all students of natural science. In it are discussed the essentials of the several topics of paramount importance, no special technical knowledge of any sort being presupposed, except on occasion.

The present work embraces a series of closely related and interdependent lectures, each of which constitutes in itself a complete unit. Repetitions were thus unavoidable; but these nevertheless may be welcomed by those who may not peruse the book in its entirety, but select for themselves such chapters as are of especial interest.

A comprehensive discussion of the subject matter is not intended. Such an attempt, without a doubt, would weary the reader, rather than exhaust the whole domain of the subject matter. This eventuality must certainly be avoided. The author desires however to stimulate the reader and thoroughly ground him in the more modern views. The choice of topics is largely a personal selection, such phases of the subject being discussed as seemed significant and productive of further development.

The author heartily acknowledges his appreciation for the assistance and the many valuable suggestions offered by Messrs. E. Madelung and W. Schütz.

WALTER GERLACH.

FRANKFORT A. M.,
March 1923.

PREFACE TO THE SECOND GERMAN EDITION

THE extremely friendly reception accorded the first edition of this book—which found expression in favorable criticism and in a rapid sale—prompted me to make no radical changes in the exposition of the subject matter. It was particularly gratifying to learn that many of my colleagues had adopted the book for their graduate students in seminar work. I am no less grateful for the many letters from colleagues commenting highly on the book; many other communications—apart from their reference to unavoidable errors—claimed a certain superficiality in treatment so much so that one good friend remarked that it appeared to him that the book was written between the hours of 2 and 4 in the morning. I hope sincerely to have overcome many of these shortcomings and yet I fear that I cannot entirely escape a similar censure; the plan and scope of the book make this very possible. In the preface to the first edition it was stated that a comprehensive discussion of the individual phases of the subject matter was not intended. The second edition will merely fill in the gaps in a provisional manner that are present in our own as well as in foreign textbooks. I do not know of any book that may possibly present to the advanced student, to the natural philosopher and to the technologist, an insight into the problems of modern physics which will ground him in the fundamentals necessary for a subsequent study of the original literature. It is a frequent seminar experience that a complete understanding and appreciation of the advances made in original research is rendered difficult not so much by the lack of knowledge of the problem itself as by an insufficient familiarity with the mode of presentation of the problem and its relationship to other problems within the scope of physics.

I have endeavored to be of service in this respect. For this reason not all the partial advances of the past two years were incorporated in the text; I have emphasized rather the fundamentals of the problems. For the same reason scant reference was made to original literature: when necessary, these may be found quite readily by reference to the few articles and authors cited in the text.

It did not prove possible to realize the original plan of the author to develop the book as a textbook of modern physics for students already versed in the general principles; lack of time and of experience prevented the fulfillment of this hope, although much work of a preliminary character has already been accomplished. If this second edition proves itself and justifies its existence, we may perhaps expand the third edition along these lines. A complete index has also been added.

I extend sincerest thanks to my colleagues, A. Landé and W. Schütz, for their many and helpful advices, and likewise to the publishers for their unstinted cooperation.

WALTER GERLACH.

TUBINGEN,
August 1926.

TRANSLATOR'S PREFACE

In presenting this translation of Professor Gerlach's excellent work, the translator has been actuated by a desire to make this clear survey of recent developments in the field of atomistics available for those who, because of their lack of German, are unable to peruse the book in the original.

The friendly reception accorded the German edition and its adoption as a seminar text book for graduate students indicate the appeal of Professor Gerlach's work alike to the chemist, the physicist, the technologist, and the natural philosopher, and is ample explanation for the appearance of this English edition.

Simplification of presentation has been sought throughout. Its phraseology has been stripped of highly technical terms, though it is neither possible nor desirable to wholly discard scientific terminology in a book of this character. However, mathematical formulation is dispensed with almost entirely, the reader being referred to original mathematical articles. The development of the several chapters is such that they are mutually exclusive and independent of one another, a feature which will appeal particularly to those who are not immediately engaged in the study of the entire field of atomistics but who will find interest in portions of the subject.

I take this occasion to express to Professor Gerlach my sincere thanks for his cooperation in making this translation possible. Grateful appreciation is extended likewise to my colleagues, Professor G. O'Grady and Dr. J. Hartmann, for invaluable assistance; and to the publishers for their unstinted cooperation and willing helpfulness.

F. J. F.

Brooklyn, N. Y.,
February, 1928.

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CHAPTER I

GENERAL ATOMISTICS

The modern conception of the atomic structure of matter is a consequence not only of the molecular theory and the theory of elements proceeding from it, but also of the kinetic theory of gases which has contributed decisively to the satisfactory explanation of Brownian Movements and the eventual confirmation of Avogadro's Law. The physical derivation of Avogadro's Law has thus reaffirmed the basic principles of chemical atomism. Our present-day knowledge rests largely upon the gradual unraveling of the inner structure of matter, the recognition of its ultimate constituents and of the forces operative within matter, their nature, origin, mutual interrelations, capabilities, etc. The various generalizations and theories, together with the necessary experimental evidences incidental to their adoption which epitomize these ideas, constitute what is commonly termed "General Atomistics."

The first period in this gradual development of general atomistics terminated brilliantly in the enunciation of the well-known "periodic system" of the elements. Through it all the known elements were capable of classification in one comprehensive scheme, the classification being based on the indivisibility of the atom and the chemical deportment of the individual elements. Forms 1 and 2 (pages 11 and 12) represent two different schemes of the periodic system, the second being especially suggestive.

The theory of the immutability of the elements, on which this first classification and the older conception of elemental substances were based, had to be abandoned on the discovery of radioactivity. Incontrovertible evidence was afforded that one element can transform itself into another, to both forms of which the concept "element" was applicable. To be sure, nature dictates precisely which elements can undergo such change, the process of change being subject in no way to the influence of exterior forces, regarding either its rapidity or the nature of the end products of the transformation. The sole visible evidence of the process itself consists in the particles ejected from the original atom, i.e., the so-called radioactive radiations. The original and final "forms" of the matter concerned and the disintegration particles ejected during change are all that is available, therefore, for the investigation of such processes.

The indestructibility of the elements being no longer tenable, the problem arose regarding the structure of the individual atoms. It became evident that only those theories of atomic structure merited serious consideration which could serve as a basis for and complement the accepted chemical system of the elements. In other words, to be acceptable, a theory must not only explain satisfactorily in the light of the individual atomic structures the chemical properties of the various elements—their similarities and their differences in behavior; but it must elucidate, in addition, the manner and process whereby elements are combined to produce molecules. Science, at present, is in the midst of this newer phase of progress and it may be predicted without fear of serious and ultimate contradiction that this, the second, stage in the development of atomistics will likewise successfully issue into another "periodic system," already indicated so definitely by the researches of Niels, Bohr, Stoner, and others.

It should be remembered, however, that the methods of investigation which reveal the details of this new system of elements differ essentially from the methods which disclosed to us the older chemical system.[1] They are based, in every case, on a recognition of the fact that atoms are composed of electro-positive and electro-negative charges. The investigation of these negative charges particularly (their origin,

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[1] See the author's "Atomic Destruction and Atomic Structure, the Physical Analysis of the Atom" (Jena, 1923, G. Fischer).

nature and mass) has been fruitful and stimulated this marked development in the study of atomism. The possibility of cleaving from an atom single electrons (i.e., to ionize the atom) with the aid of energies whose order of magnitude is comparable to the energy involved in chemical reactions, and the subsequent demonstration that the atom, after loss of these electrons, remained as the "positive ion" of the otherwise unchanged element, indicated unmistakably the presence of electrons within the normal atom. However, the number of electrons residing, as essential constituents, within the several atoms was at first not known. Since the atom, per se, is electrically neutral, it follows, a fortiori, that within its interior are confined unit charges of positive electricity, whose number must be exactly as large as that of the negative charges or electrons, within the atom. On the other hand, the isolation of "mass free" positive charges, i.e., their separation or cleavage from matter, has never been accomplished. Indeed, wherever positive charges have come under observation they have been found always in conjunction with, and associated with, atoms. Since, moreover, the elements retained their respective masses intact after ionization, i.e., after experiencing a loss of one or more electrons, and remained chemically unaltered, it was only logical to infer that positive charges are coupled with and are part of the residual "material" mass of the elements—a bond which seems essential to their very existence. The lightest known atomic mass is that of the hydrogen atom. When this is ionized, i.e., when it has lost an electron, it is to be assumed that the residual mass, the positively charged hydrogen ion, represents the smallest unit mass of positive electricity. Again, since all attempts to withdraw more than one electron from the hydrogen atom always have proved futile, it was definitely established that the neutral hydrogen atom is composed of one unit positive charge associated with the atomic mass and one electron. Obviously this positive hydrogen residue is the ultimate atom of positive electricity itself.[2]

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[2] (At a meeting of the British Association held at Cardiff in 1920 E. Rutherford suggested that this unit positive charge be named "Proton.") Tr.

Further progress in this general direction was achieved by the researches of Lenard and Rutherford on the penetrability of matter by electrons and alpha particles respectively. Inasmuch as alpha particles have been shown to be identical with positively charged helium atoms, corpuscular rays (helium atoms) have been utilized, and they serve efficiently as a new means for investigating atomic phenomena with especial reference to atomic structure. Experiments have demonstrated that alpha rays, in their passage through matter (gaseous or solid bodies), are so emphatically deflected from their original path that they may be propelled actually in a direction opposite to their initial direction. This phenomenon is called "scattering." Rutherford explained this peculiarity as due to the electrostatic deflecting force experienced when electro-positive alpha particles approach very closely to the electrically charged atomic mass. Since this phenomenon is obviously of but rare occurrence, the unavoidable conclusion was reached that positive electric charges together with the atomic mass were concentrated in an extremely small portion of the atom, in a minute central region—its so-called "nucleus." Then, too, the differing extents of deflection produced by different atoms were explained by assigning to atoms of increasing atomic weights a corresponding increase in the number of its positive charges. The central nucleus of the several atoms therefore contains all their positive electricity and their respective mass. Through such results the essential tenets of the modern nucleus theory (as formulated in 1911 by Rutherford) were acknowledged and eventually accepted.

However, a result remarkable for its astonishingly quantitative significance was soon forthcoming. It was observed that the net nuclear charge of an atom, that is, the number of the unit positive charges centralized at the core of the several atoms as determined by alpha ray deflections, increased with ascending atomic weights of the respective elements, their charge being equal roughly to one-half the atomic weight. Hence it was suggested by van der Broeck that the number of charges upon an atomic nucleus is comparable to the "position number" of the element in the "periodic system." The numbers marked Z in the subjoined table of the periodic system designate these "atomic numbers." For the sake of completeness it may not be inappropriate to state here that the critical investigation by Moseley[3] of the X-ray spectra (produced by the various elements when used as anticathodes of a discharge tube) has revealed as a characteristic for each element the same number of charges as are indicated by alpha ray experimentation. This statement is not unfounded. Subsequent investigators confirmed this work of Moseley, notable among them being Chadwick[4] who successfully determined atomic number to within one per cent by means of alpha ray measurements. Again the obvious electrical neutrality of the normal atoms necessitates the conclusion that the electrons residing within the several atoms are equal in number to this "atomic number" or nuclear charge of the respective atoms. These electrons are localized within the atom in definite positions in concentric circlets about the positively charged nucleus, each atomic type being characterized by a definite geometric configuration. The principles of modern atomic physics and their eventual successful adoption are based largely on the knowledge gained by these observations.

Coincident with this newer progress keen interest was focused upon the century-old, but discarded, hypothesis of Prout—the most prominent unitary theory of matter—according to which all elements are more or less complex aggregates of the element hydrogen, the latter assuming the rôle of a quasi-primordial substance. We shall discuss this theory more fully in the following chapter. We are here concerned with one point only. Granting, first, the identity of the hydrogen ion and the unit positive charge (proton) and, secondly, the equality between the number of positive

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[3] Phil. Mag. 26, 1031, 1913. "The result of this piece of work, now classical, was the establishment of the most important generalization in the history of chemistry since Mendeleef's Periodic Law." Aston in his book on Isotopes. Tr.

[4] Phil. Mag. 40, 734, 1920.

charges residing within the several atoms and the atomic numbers of the respective elements, it would seem to follow logically that the atomic weight of a given element should equal its respective atomic number. Yet in not one instance has this equality been established (with the noteworthy exception of hydrogen itself), the former proving greater than the latter for all elements. In other words the number of "mass units" constituting an atom is always larger than the number of its positive charges. To explain this seeming discrepancy and yet maintain a firm and intimate association —actually an identity—of atomic mass and positive charge, it is but necessary to assume that the atomic nucleus comprises as many "mass units" as are indicated by the atomic weight and in addition units of negative electricity (electrons) equal in number to the difference between the atomic weights and the atomic numbers of the respective elements; these factors determine the constitution of the atomic nucleus. Such a supposition is indeed reasonable inasmuch as radioactive phenomena time and again have evidenced atomic disintegrations during which an emission of electrons, as β-rays, takes place. Again, such disintegration entirely alters the chemical characteristics of the original element, giving rise simultaneously to the formation of a new element. Obviously, then, the nucleus of the disintegrating atom and not its planetary electronic shells must be the source of these emitted electrons (β-rays), since it is the nucleus which determines the chemical character and nature of an element. As already noted, the mere cleavage from a substance of an extra-nuclear electron (i.e., ionization) in no wise affects the chemical identity nor does it influence the chemical deportment of the original substance. The peculiar nature of such disintegration process and the chemical relations of the new element formed during such a transformation to its parent element gave rise to the extraordinarily ingenious and important "Radioactive Displacement Law of Fajans and Soddy."[5] Thus the question of "charge" presents no serious and insurmountable difficulty to the hypothesis of Prout.

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[5] The reader is referred to Fajans' "Radioactivity" (Vieweg, 45).

Further progress of such epoch-making and revolutionary discoveries undoubtedly would have ceased at this point had not the timely researches of Niels Bohr revealed fine and more subtle details of the structure of the atom. The emissions produced by atoms—previously stimulated to glow—were ascribed for a long time to the presence of electrons within the atom. This conception was accepted and established as correct when spectroscopic examination (particularly the observation of the alteration of the wave-length of light emitted by glowing bodies when under the influence of magnetic forces, the so-called Zeeman Effect) made it possible to determine the specific charge of an electron and subsequently to demonstrate the exact equality of this charge to the corresponding values obtained for free electrons in cathode rays. An almost immediate consequence of this quantitative finding is the knowledge of the complete similarity of electrons within and without the atoms, of free electrons and atomic electrons as well as of nuclear electrons, since the same value is obtained for the charge on β-rays produced during radioactive decay. Hitherto, line spectra were explained on the basis of certain very plausible assumptions by the aid of which the wave-lengths of the hydrogen spectral lines and some helium lines could be exactly computed. These fundamental assumptions are: the application of the planetary laws to the movements of the several constituents of the atom, and secondly, a very definite arrangement of the electrons within the atom. To these are added the two assumptions regarding emissions which have been adopted as axioms of the quantum theory. These will receive fuller discussion in a later chapter. Upon them rests the entire foundation of modern atomism (to a discussion of which this volume is committed), whose prime purpose is to unravel the mysteries of matter: the inner structure of the atom, the laws of the forces operative within and without the atom.

As stated above, as soon as these perplexities have been solved we shall witness the gradual close of the second stage in the development of the general system of the elements. In the main, the completion of this period is already at hand. The elaboration however of a system of mechanics valid for such a system of charges still remains to be accomplished. The question of the structure of all atoms is still unanswered. The third stage of this newer progress is even now in marked evidence and its first success—we may say, the very first—viz.: the structure of the atomic nucleus, fully achieved. Two atomic constituents (or atomic bricks), the positively charged mass particles (hydrogen nucleus) and electrons, are already definitely known to us. On the other hand, radioactive phenomena demonstrate that such atomic disintegrations as accompany the emission of alpha-particles likewise give rise to helium atoms carrying double positive charges as an end product. These also must be considered, in some form or other, as constituents of atoms, at least of radioactive atoms. Even though the helium atoms, in turn, are composites of hydrogen nuclei and electrons, they are endowed with an exceedingly firm and mutual bond of attraction which imparts to them the nature of independent and self-subsisting constituents. A more penetrating and a more elucidating insight into this phase of atomic structure may confidently be expected from the recent work of Rutherford who succeeded in disrupting elements, that is, in decomposing atomic nuclei into their prime constituents. A separate chapter (Chapter V) will be devoted to this atomic disruption.

There remains one more point for discussion. Granting the necessary existence of nuclear electrons to compensate for the difference between atomic weight and atomic charge, experiment reveals that not all elements possess atomic weights which are whole numbers or multiples of the mass of the hydrogen atom. This observation in no way conforms to the hypothesis of Prout. Atomic weights of the several elements, based particularly upon that of hydrogen (*Prout's protyle*) as unity, plainly indicate fractional values in nearly all instances. Primarily for this reason the atomic weight of oxygen has been accepted as 16.000. On this new scale the atomic weight of hydrogen becomes 1.008, a fractional number, whereas the atomic weights of many other elements (which are fractional on the basis of hydrogen equal to 1) become whole numbers. However, two accomplishments of modern physics have opened a new vista that apparently leads to fairly unmistakable conclusions. These are: an experimental point of view and a theoretical point of view, both of which offer ready explanation for the phenomenon of uneven atomic weights even if the hydrogen ion is adopted as the basic material constituent of atomic nuclei. A few words will make this clear.

Radioactivity has unearthed a great number of chemical elements for which the periodic system of elements offers apparently no assignable and available place. Examination of the chemical properties of these elements, however, has forced the assumption of the possibility for the one and the same place in the periodic system to accommodate, and therefore be assignable to, several elements which may be entirely similar chemically and which possess the same atomic number, but which are characterized by different atomic weights. The nuclei of such elements are similar exteriorly, i.e., as regards the number of their electric charges; on the other hand, the number of positive mass units and electrons contained within their interior are different. We may distinguish two cases: either the number of "mass units" is the same and the nuclear electrons different, or the number of "mass units" as well as the number of the nuclear electrons may be different. In both cases the net positive charge resulting from the number of "mass units" less the number of nuclear electrons always remains the same. Such elements are termed "isotopes." We need make but one assumption, an assumption that formerly appeared audacious but has now proved correct, viz.: that isotopes occur at many places in the periodic system; recent investigation has demonstrated this assumption to be capable of verification. In other words, "isotopes" are not the isolated consequences of purely radioactive processes but rather products of a transformation phenomenon common to, and inherent in, most if not all our so-called elements. There are, therefore, certain "elements" which we recognize and accept as true elements according to all our present chemical standards but which in reality are mixtures of several atoms similar in all things chemical but possessing different masses. In the next chapter we shall consider more fully this phenomenon of the general isotopy of the elements together with some of its obvious effects upon our concept of "chemical element."

The second reason, a theoretical one, for the phenomenon of fractional atomic weights follows from the relativity theory, from the equivalence of energy and mass. If energy is endowed with mass, it is possible for atomic nuclei constructed from "n" units of mass to possess an atomic weight entirely different from "n" provided the energy of combination of the "n" units in the nuclei is sufficiently large. Although we shall learn in the following chapter that almost all uneven atomic weights are explainable by means of general isotopy, nevertheless we may state here that the atomic weight 1.008 for hydrogen instead of 1.000 is not due to any isotopy of the hydrogen atom. The influence of the mass of nuclear energy, as thus proposed by the relativity theory, may have a bearing upon this question as well as upon the case of helium.

Furthermore, the study of the classification of the elements and speculation as to atomic structure are of importance also to theoretical atomic physics. Thus, the physical order of the elements has disclosed evidences that the anomalies in the atomic weights of several elements, e.g., cobalt and nickel, due to their relative positions in the periodic arrangement of the elements, do not signify an anomaly in their respective atomic structures. On the other hand, the physical order of the atoms arranged according to their respective atomic numbers corroborates the arrangement of the elements predicated upon their chemical character.

The heuristic merit of the atom-theory is accentuated especially in the discovery of new elements. Until rather

THE PERIODIC SYSTEM OF THE ELEMENTS.

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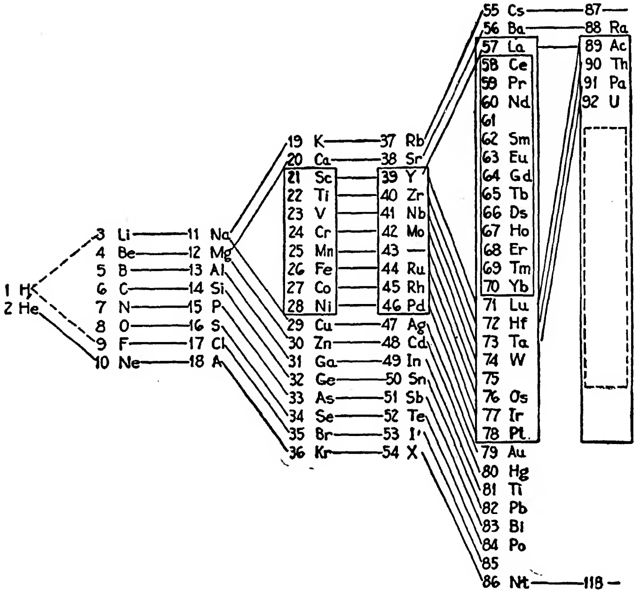
Period.	Series.	Group. 0.	Group. VIII.	Group I. a	Group I. b	Group II. a	Group II. b	Group III. a	Group III. b	Group IV. a	Group IV. b	Group V. a	Group V. b	Group VI. a	Group VI. b	Group VII. a	Group VII. b
I.	1	2 He 4·00		3 Li 6·94		4 Be 9·1		5 B 11·0		6 C 12·00			7 N 14·01		8 O 16·00		9 F 19·0
II.	2	10 Ne 20·2		11 Na 23·00		12 Mg 24·32		13 Al 27·1		14 Si 28·3			15 P 31·04		16 S 32·06		17 Cl 35·46
III.	3	18 A 39·88		19 K 39·10		20 Ca 40·07		21 Sc 45·1		22 Ti 48·1		23 V 51·0		24 Cr 52·0		25 Mn 54·93	
	4		26 Fe 27 Co 28 Ni 55·84 58·97 58·68		29 Cu 63·57		30 Zn 65·37		31 Ga 69·9		32 Ge 72·5		33 As 74·96		34 Se 79·2		35 Br 79·92
IV.	5	36 Kr 82·92		37 Rb 85·45		38 Sr 87·63		39 Y 88·7		40 Zr 90·6		41 Nb 93·5		42 Mo 96·0		43 –	
	6		44 Ru 45 Rh 46 Pd 101·7 102·9 106·7		47 Ag 107·88		48 Cd 112·4		49 In 114·8		50 Sn 118·7		51 Sb 120·2		52 Te 127·5		53 I 126·92
V.	7	54 Xe 130·2		55 Cs 132·81		56 Ba 137·37		57 La 139·0		58 Ce 140·25		59 Pr 140·9	60 Nd 144·3	61 –	62 Sm 150·4	63 Eu 152·0	
	8	64 Gd 157·3	65 Tb 66 Dy 159·2 162·5	67 Ho 163·5	68 Er 167·7		69 Tu I. 168·5	70 Yb 173·5	71 Lu 175·0	72 Tu II		73 Ta 181·5		74 W 184·0		75 –	
	9		76 Os 77 Ir 78 Pt 190·9 193·1 195·2		79 Au 197 2		80 Hg 200·6		81 Tl 204·0		82 Pb 207·20		83 Bi 208·0		84 Po (210·0)		85 –
VI.	10	86 Nt (222·0)		87 –		88 Ra 226·0		89 Ac (227)		90 Th 232·15		91 Pa (230)		92 U 238·2			

Atomic numbers are placed before the symbol of each element, atomic weights below. Between thallium (81) and uranium (92) almost every place in the system contains several elements, for the most part radioactive. The symbol and atomic weight of only the longest lived (i.e. most widely distributed) member of each "Pleiad" is given. The bracketed atomic weights of Po and Nt are determined by calculation, while those of Ac and Pa are hypothetical (according to Fajans). The bracketed numbers below Na, Ce and Ag are new precision measurements of O. Hönigschmid.

recently, elements of the ordinal numbers (i.e., serial or placement numbers in the order in which they occur in the periodic system) 43, 61, 72, 75, 85 and 87 were still unknown. There was also considerable doubt as to the true natures of the elements No. 71 (lutetium) and No. 72, the latter being entirely unknown at first. Both were assigned to the group of so-called "rare earths." The arrangement of the periodic system (form 2) indicates unmistakably and clearly, however, that lutetium belongs to the Scandium-Ytterbium series of elements, whereas the element No. 72 is a member of the series Titanium-Zirconium. The discovery of this latter element by Coster and Hevesy is especially worthy of mention. Element No. 72 is the recently discovered element hafnium (Hf) named in honor of the place of its discovery, Copenhagen (Hafnia). On the basis of its position in the periodic scheme of elements as pictured in form No. 2, it was but natural to infer that hafnium (No. 72) is similar in chemical character



Bohr's System of the Elements

to zirconium. This inference was the determining factor in devising chemical methods for the systematic search for this element. Its eventual discovery, however, was accomplished not by chemical methods, but by the much simpler X-ray spectral analysis. Coster detected in the X-ray spectra of zirconium minerals a number of spectral lines which were not attributable to any known element but whose wavelengths on the contrary indicated the presence of an element of atomic number No. 72. Following thus upon its discovery, Hevesy succeeded in separating the new element from zirconium by purely chemical manipulations upon minerals whose hafnium content had been shown to be especially high by means of X-ray analysis. Among the pieces so treated was a specimen of "pure zirconium." Thus the discovery of the new element hafnium serves as a typical instance of the direct and practical utility derivable from a theoretical conclusion and at the same time it points out the importance of our modern experimental methods. Without this theoretical viewpoint as a guiding or directing principle, it would have taken, undoubtedly, a much longer time to demonstrate that "chemically pure" zirconium still contained several per cent of another element. Honigschmid subsequently determined the atomic weight of hafnium to be 178.3.

After many preparatory experiments, which are founded more or less completely upon the work of V. M. Goldschmidt, there were found within recent years the two homologues of manganese of atomic numbers respectively 43 and 75 (eka-manganese). These experiments were carried out by Berg, Tacke and Nordack in the physical laboratory of Siemans and Halske. In this instance, also, the decisive step of the discovery was brought about by X-ray spectral analysis. Not only by means of it was the existence of these elements definitely established, but it showed likewise the success of chemical concentration methods. Element No. 43 was named masurium (Ma) and No. 75 was given the name rhenium (Re).

Although the scientific, heuristic and practical utility of modern atomic theory may be appreciable, yet it cannot be denied that at this very time the theory is undergoing a severe crisis. The present state of "general atomistics" is characterized by the uncertainty of the mechanical explanation of atomic and inter-atomic processes; indeed it even questions the justification of an attempt at such an explanation. Hitherto, mechanics was deemed fundamental in the considerations of the reciprocal action of the atoms with one another and of the reactions taking place within their interior. In fact Bohr's theory unquestionably owes its first great success to that ingenious combination of mechanics and the quantum theory of which we will learn more fully in the chapter on the magneton and especially in that which deals with the spectrum of hydrogen. All attempts to arrive at a comprehension of the distinctive details have proven futile thus far, even the most simple determination of the stability of an atom, the calculation of its ionization potential, having failed. Upon reflection this should not be surprising. Investigation of atomic structure is so intimately correlated with the quantum theory that solution of the one is not possible without simultaneous solution of the other. Indeed, the fundamental experiment upon which the whole modern quantum theory has been developed (the Frank-Hertz experiment on the excitation of atoms with the production of radiation by means of electronic impacts) is a non-mechanical process. A considerable portion of the "perplexing puzzle" of the quantum theory results from the peculiarly "selective transfer" of an impacting electron's energy of motion into the potential energy of the impacted atom, which takes place only when the electron possesses a certain minimum or critical velocity which varies from atom to atom; for all other velocities of the electron, the impact is considered elastic, i.e., it takes place without such an energy transfer. Experimental observations of this nature lead to a somewhat depressing conclusion, viz.: for the present, it seems impossible for us to devise an experiment to investigate the changes taking place within the atom. If we were desirous of investigating the path of an electron more or less quantitatively, we could conceive for convenience "electronic probes" with which we could examine both the "temporal and spatial" motion of the atomic electron. But such a plan would not be feasible, since the reciprocal interaction between an atomic electron and an exterior electron brought into close proximity with it is governed by the self-same quantum laws whose intrinsic nature we wish to investigate. The quantum theory obviously cannot be proved upon its own assumptions.

At this time, Born, Heisenberg and Jordan on the one side and E. Schroedinger on the other are fruitfully studying these problems. The latter has succeeded in formulating a new general mechanics, "Undulation Mechanics," whose physical merit has already been evidenced. These questions, however, are still so indefinite and shrouded in uncertainty as to preclude discussion of them at this point.

CHAPTER II

ISOTOPY

We have observed in the course of the discussion on general atomistics how the concept of "isotopes" arose and evolved from the consideration and study of the disintegration and transformation processes taking place within "radioactive" substances. We will discuss more minutely the modern atomic weight determinations which sponsor the view that isotopy is an important phenomenon of common rather than uncommon occurrence. Isotopic elements, to the fullest of our knowledge, are such elements which are not separable, and therefore not distinguishable, by any known chemical methods, but may be differentiated by means of important physical properties, e.g., mass and spectra. Since their chemical separation is thus not possible, it would be futile to attempt atomic weight determinations based upon purely chemical processes. There are, fortunately, a number of physical phenomena whose quantitative measurements are influenced only by their respective masses. Only such phenomena may be utilized efficiently in the separation of isotopic elements. We shall revert to this later for fuller discussion.

Physics presents and makes available a method capable of distinguishing and separating individual atoms according to their respective masses; and even though the "yield" of this method, estimated in quantities of isotopes actually separated, is very small, still its scientific accomplishment is extraordinarily extensive and its possibilities are by no means exhausted. The method in question is based upon the magnetic and electric deflections experienced by charged particles while in motion. From these deflections, we may compute the value of the ratio of charge to mass, e/m. Mass particles of the smallest possible magnitude and endowed with similar charges are available for experimental study in the so-called "canal rays" or "positive rays," first observed as a luminous stream by Goldstein in 1886.

Canal rays result whenever a discharge takes place in Geisler tubes filled with an inert gas at a diminished pressure. Owing to the electric discharge, ionization of atoms takes place, i.e., they disrupt and split up into smaller fragments, into positive gas-ions and (negative) electrons. The latter are repelled electrostatically from the cathode; the former, the positive ions, are urged toward the cathodes and impinge upon it, releasing from the cathodic material, as result of the impact, the electrons requisite for a constant electric discharge. If the cathode is perforated with one or more openings (Kanalen), those ions, which are being propelled toward it along the axis of one of these openings, obviously will travel through the cathodic perforation *in a direction away from the anode*, and become observable behind the cathode.[1]

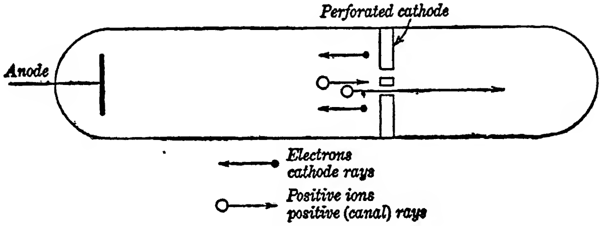


FIG. 1.

They will continue in a rectilinear direction with constant velocity so long as their motion is not affected by impacts with other gas-atoms. Along this path they are readily investigable and susceptible to experimentation. They may be subjected to exterior forces and the effect therefrom upon their motion—direction and velocity—easily determined. Since they are electrical charges in motion, they constitute an electrical convection stream capable of deflection[2] by

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[1] Hence the name of "Kanalstrahlen" or "Canal Rays." Tr.

[2] Wien, Verh. d. Phys. Gesell. 17, 1898. Tr.

means of a magnetic field while the charges themselves will suffer deviation from their normally straight path by electrical fields.[3] The type of deflection depends upon the nature of the force, magnetic or electric; and its magnitude upon the mass, charge and velocity of the "canal rays."

When these moving particles are subjected to the simultaneous action of a magnetic and an electric field, they experience deflections which give rise to the well-known "Thomson parabolas." Positive rays of various types, but of equal velocities, i.e., such as possess similar charges and dissimilar masses or similar masses and different charges, are so deflected under these conditions that particles characterized by an equal *e/m* ratio will converge to the one and same point of a conveniently placed sensitized screen.

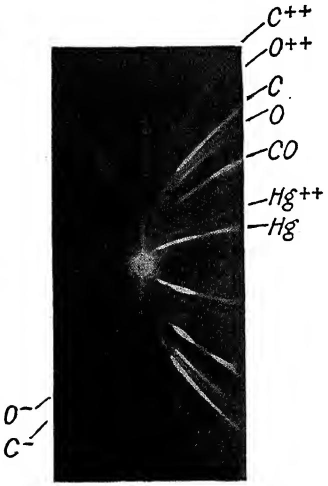

FIG. 2.

It may be expected that all particles of equal *e/m* should be thus deflected to a single point whereas photographic records indicate parabolic curves. This undoubtedly would result if all positive rays were moving, at the time of deflection, with equal speeds. Evidently this is not so, as is demonstrated by the "spreading" of the parabola, which indicates a sorting of the particles by the impressed fields according to the particles' respective speeds.

The presence of these rays may be detected by the phosphorescence produced by them when they impinge upon certain substances,[4] as glass or the mineral willemite, or by

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[3] The direction of this deflection indicated electrification opposite in kind to that of the "cathode rays." Hence J. J. Thomson proposed their classification as "positive rays." J. J. Thomson, "Rays of Positive Electricity," Longmans, 1921. Tr.

[4] The color emitted by the object during phosphorescence is variable depending upon the nature of the body; e.g., in the case of willemite, a low faint green is obtained.

their effect upon photographic plates. The latter phenomenon may be designated as a "druckbelichtung." Just as mechanically pressed photographic plates show upon development a "darkening" at the points of compression, so do these speedily moving particles impinging with great energy upon an exposed plate produce a similar effect, that is, their points of incidence show as "darkened points of pressure." Again, as happens in photography, the entire silver bromide granules are developed even though but one molecule of the bromide may have been altered. Photographic plates especially adapted for positive ray investigation because of their extreme sensitivity have been prepared by V. Schumann (the so-called Schumann plates). These are gelatine-free (or of a minimum gelatine content) silver halogen plates prepared by Schumann to obtain photographic evidence of extremely short-waved radiations which are absorbed in the gelatine film of the ordinary plates.

Inasmuch as the principal purpose of positive ray analysis is the direct determination of atomic and molecular masses, this parabolic "spreading" carries with it a decided disadvantage. The decrease in intensity of the curve as it extends away from the origin would be obviated if all particles of equal e/m value, irrespective of variable velocity, were deflected to but one point. Then, too, the impressions are not sharply defined but more or less blurred, due to the masking produced by umbra and penumbra effects.

This interference on the part of the variable velocity of the particles was soon overcome by F. W. Aston who was the first to realize that all particles characterized by an equal e/m ratio may be focussed to a single point upon the film even though endowed with different velocities. Hence the eventual deflection of the ray depends solely upon the relation "charge to mass" (e/m). This concentration, or restriction, of the particles of a stream to a single point is

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The capability to produce phosphorescence has revealed that these rays are normally propagated in a rectilinear path. This may be confirmed by the shadow cast of the glass of the discharge tube when a solid body is placed in the path of a pencil of positive rays. Tr.

accomplished readily by permitting the rays to pass successively through electric and magnetic fields placed at right angles to one another. In this way the "velocity spreading" occasioned by the electric field is reversed by the magnetic field. Obviously, the intensity of the impression produced by such a ray becomes rather great if all its particles become concentrated in one point. In this manner the weakening in intensity due to the spreading of the particles over a parabolic arc is avoided. It thus becomes possible to utilize beams of positive rays of rather narrow cross section and to receive upon the sensitized plate a proportionately sharp impression. This is especially interesting since a pronounced falling off in the intensity of the Thomson parabolas takes place if one attempts to make them finer in order to increase the accuracy of subsequent measurements. In each case, also, the photograph will depict the mass spectra of the gas under investigation. This emphatically suggests the feasibility of separating particles of very nearly equal e/m values and of measuring them exactly and subsequently of comparing the respective deflections of these particles.

The following figure (Fig. 3) illustrates the essential experimental points of the mode of procedure adopted by Aston, the theory of which is published in detail in the Philosophical Magazine, May 1920. B is the discharge tube, analogous to an ordinary X-ray bulb, positive rays originating from the cathode C, entering through the slits S_1 and S_2 into the electric field between J_1J_2. L is a stopcock by means of which the camera OZ is cut off from the discharge tube. M represents a cross section of the magnetic field whose lines

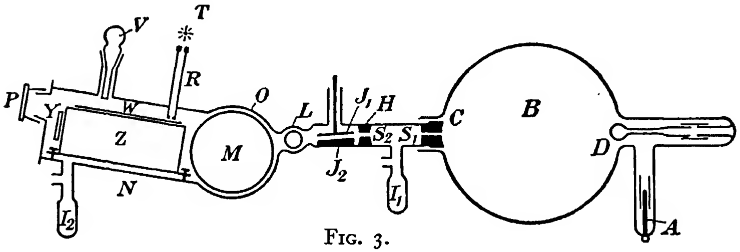


Fig. 3.

of force run perpendicular to the plane of the diagram. Z is a support which holds the photographic plate W upon which the canal rays impinge following their magnetic deflection.

Figure 4 indicates the path of the rays. After being sorted out into a narrow beam by the two parallel slits S_1 and S_2, positive rays enter into the electric field E, impressed upon the plates P_1 and P_2. Here the beam is deviated, as shown, through an angle θ; at the same time it spreads into an electric spectrum due to the dispersion of the component rays of different energies. A selected part of this spectrum is transmitted by the diaphragm into the magnetic field generated by a powerful electromagnet, whose poles are designated by the circle O. The direction of the magnetic field is such as to bend the rays in the opposite direction through an angle ϕ larger than 2θ. As a consequence the dispersed rays having a constant e/m ratio will be collected and made to converge to a focus at F. If a photographic plate is placed at GF so that its prolongation makes with the initial direction of the beam the same angle θ, it may be shown that all the rays of equal e/m ratio will come to focus at one point. Upon development, therefore, such a plate will exhibit a series of lines, each one corresponding to a definite e/m ratio. In other words, a spectrum dependent solely upon the mass of the particles is obtained. Such a spectrum may be termed appropriately a "mass spectrum."

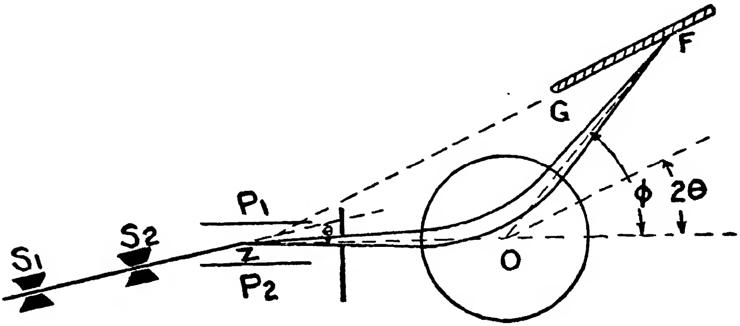
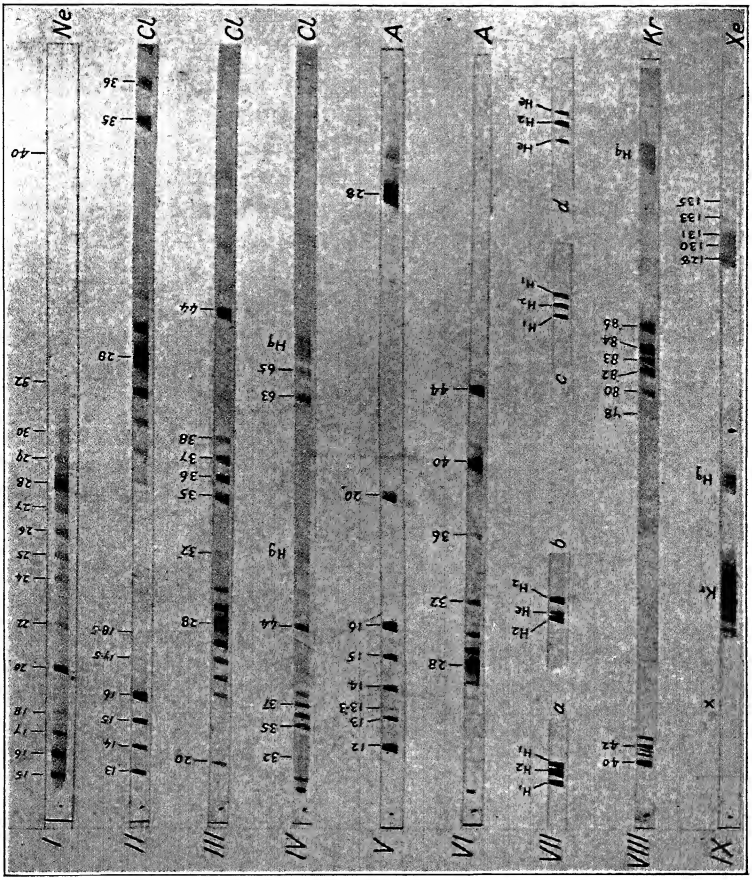


FIG. 4.

Using this focus method Aston investigated a large number of elements in order to determine their atomic weights. The availability and eventual choice of elements for such a study are limited, however, since only such may be selected as lend themselves in gaseous form to examination as positive rays. This would apply without fail for the gaseous elements and for such other elements that are characterized by a sufficiently high vapor pressure at normal temperatures, e.g., bromine and iodine. Finally, the examination also proved successful for those elements which formed compounds possessing relatively high vapor pressures at normal temperature. Tin tetrachloride may be cited as an example.

Dempster soon thereafter adopted Aston's method to examine anode rays, which likewise are positively charged particles. It was known that heated salts emit positive ions. Anode rays are (according to Gehrcke and Reichenheim) rapidly moving positively charged particles ejected from anodes at elevated temperatures. Thus, using this modified Aston method, rays of positively charged metal ions may be obtained in rather high concentration from anodes impregnated with salts. The alkali metals and magnesium were thus subjected to successful measurements.

Figure 5 depicts a few of Aston's results. Each spectrum indicates the composition of the gaseous substance, every line as stated above representing a definite relation e/m. A cursory examination will disclose very positive e/m values for all cases, and furthermore, since the ion charge e may be set constant, it follows that the corresponding m values are all fixed and determined. The m values, so obtained, designate the several atomic weights based upon any arbitrarily selected scale. It is noteworthy that all these numbers are whole numbers and not in one instance does a fractional atomic weight occur. It is apparent, too, that many more masses "m" are differentiated and designated in these spectra than are accounted for by the so-called known "elements." Strange to say, the plate (which is typical of all Aston's results) reveals more than one, two or even more mass or


I Ne
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16
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32
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II Cl
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16
17·5
18·5
28
35
36
III Cl
20
28
32
35
36
37
38
44
IV Cl
32
35
37
44
H₉
63
65
H₉
V A
12
13
13·3
14
15
16
20
28
VI A
28
32
36
40
44
VII
H₁
H₂
H₁
a
H₂
He
H₁
b
H₁
H₂
H₁
c
d
He
H₂
He
VIII Kr
40
42
78
80
82
83
84
86
H₉
IX Xe
×
Kr
H₉
128
130
131
133
135

Fig. 5.

"*m*" values which differ from one another by one or two units—not by fractions—for just those elements which are characterized by fractional atomic weights as ordinarily accepted. Wherever, therefore, the ordinary "chemical" atomic weight departs markedly from a whole number, it may be inferred, from Aston's results, that the atoms of such elements are comprised of two or more isotopic atoms each being characterized by a whole number atomic weight, their average giving rise to the ordinary atomic weight as used in chemistry. For example, the ordinary chemical atomic weight of chlorine is 35.46, a pronounced departure from whole numbers. With phosgene gas (COCl) as the gas under investigation the photographs obtained are shown in spectra 2, 3, and 4. These are characterized by four very sharp and definite lines, corresponding to the positions 35, 36, 37, 38, all placed to the right of the position 32 (O_2). Faint lines are also observed at the positions 17.5 and 18.5. However, these appeared only when chlorine was introduced into the apparatus. The only logical inference is that chlorine is a mixture of two chemically similar chlorine atoms, but of different masses. In other words it is isotopic in nature, its isotopes having the masses 35 and 37 respectively. The interpretation of the lines 36 and 38 will be discussed later. In this way the phenomenon of general isotopy was confirmed and the proof brought forth that those "elements" for which experiment has demonstrated fractional atomic weights were not "simple" but in reality mixtures of several "elements," chemically similar but different in their mass. This method, because of its nature, is designated "Mass Spectrography" and the instrument a "mass spectrograph."

A word more regarding the manner of evaluating and interpreting such positive ray spectrographs. Its basis is entirely empirical. Photographs are obtained with certain selected "simple" elementary gases confined in the discharge tube. Or compounds may be selected whose molecules are composed of such "simple" elements. A second exposure, with the unknown substance in the discharge tube, is then made upon another section of the same plate. The mass of the "unknown" is thus determined from its relative position to the "fixed masses" of the simple elements. Such "norms" or reference lines are obtained with the following substance.

C	CH	CH_2	CH_3	CO	CO_2
12	13	14	15	28	44

When calculated in this manner, the mass of the unknown, in turn, may serve as a new "reference" for further measurements.

If for the moment we confine our special attention to individual data gleaned from investigation carried out to date, we may construct the following table of the so-called "pure" or "simple" elements, i.e., elements of whole-numbered atomic weights. Hydrogen was found to be not composite; it was easy to show that its atomic weight is not 1.000, but somewhat greater than 1.000, a proof of the correctness in the selection of oxygen = 16 and hydrogen = 1.008, as atomic weight standards, a choice previously made merely because of convenience.

A detailed discussion of Fig. 5 will not be undertaken at this time. We may mention, however, that together with chlorine Cl = 35 and Cl = 37, that is, chlorine atoms of atomic weights 35 and 37 respectively, there were also found lines at 36 and 38, corresponding to HCl_{35} and HCl_{37}. The fact that negative chlorine atoms yielded only the two points 35 and 37 indicates without doubt that these lines (36 and 38) do not designate chlorine isotopes, but the hydrides of Cl_{35} and Cl_{37} corresponding respectively to the masses 36 and 38. Furthermore there are obtained—less frequently to be sure—atoms carrying a double charge, i.e., atoms with the ratio $2e/m$ or $e/\frac{1}{2}m$; in the case of chlorine, as stated above, these would be $35/2 = 17.5$ and $37/2 = 18.5$. That there are but two isotopes of chlorine seems to be borne out by later work of Aston in which it was shown that only the lines 35 and 37 could be distinguished in negative mass spectra. As an added evidence that these are the chief, if not the only, isotopic constituents of chlorine, attention may be drawn to the points 63 and 65, corresponding respectively to $COCl_{35}$ and $COCl_{37}$. (See spectrum 4.) The proportions of the several isotopes in a mixture may be estimated readily by the relative intensity of the respective "mass points." In this manner values are obtained which are in accord with the proportions of the atomic components as computed from the atomic weights. Details may be gathered from the table.

A noteworthy fact is the large number of isotopic components of the "higher" elements. Investigations now being made will probably provide in the near future an explanation for this phenomenon. The question regarding the existence of "isobars" will receive but passing consideration. Our present knowledge of this phase of the subject matter is too limited and not sufficiently clarified to warrant extensive comment. Suffice it to say, at this point, that isobars are elements of equal mass, but differentiated as regards their chemical nature and deportment. Examples of this type are (as given in the table): argon and calcium with atomic masses of 40; zinc and germanium (mass 70); germanium and selenium (mass 74); selenium and kryton (mass 78, 80, 83); rubidium and strontium (mass 87). The first set of isotopes (A_{40} and Ca_{40}) have been investigated by Aston in an especially painstaking experiment and their perfect equality in masses demonstrated. The possible difference in the respective masses of these two elements is less than 1 part per 1000. This subject leads us to that of the physics of the atomic nucleus, which is, at present, in a very rudimentary stage.

We may ask, furthermore, how closely do the masses of these isotopes approximate whole numbers? Do deviations occur as in the case of hydrogen? Undoubtedly so! But it is very surprising, indeed, that such deviations are observed only for the "heavier" elements and not for the "lighter" atoms. Thus, the average masses obtained from several different measurements for the lithium isotopes were 6.008

± 0.005 and 7.006 ± 0.005; for beryllium 9.002, within the same degree of accuracy as the above. On the other hand, the mass of strontium (88) is considerably less than 88, viz.: 87.8. Similarly the mass of the barium atom is 137.8 and not the whole number 138. For the moment, therefore, we must consider the masses of the lithium isotopes as whole numbers.

It is worthy of note also that these "mixed elements"—with the possible exception of several lead isotopes resulting from relatively rapid radioactive disintegration processes—should always possess the same atomic weight, as obtained chemically, irrespective of the source or the previous history of the "element." Evidently, therefore, these mixed elements are formed in nature with a constant proportion of their respective components. Explanation for this phenomenon is still lacking. It is reasonable indeed—and feasible too—to conceive of an equilibrium in nature which corresponds to the equilibrium of radioactive phenomena and which originated in a manner analogous to radioactive equilibrium, and to assume, further, the formation of isotopes to be a consequence of several radioactive disintegration processes of "higher" elements, whose end products depend largely upon the nature of the process. This would mean that these "elements" are decomposition products of "higher" (or more complex elements), rather than complexes synthesized from "lower" (simpler) constituents. Of course the possibility still exists that a synthesis of the "higher" elements may also take place in accordance with similar laws of probability as those governing spontaneous disintegration. But as yet no evidence of such a process exists.

The several vertical columns of the subjoined table present respectively the following data: the atomic or ordinal number of the element, its name, symbol, chemical atomic weight, the number of known isotopes (given as a minimum, since these are easily verifiable), the masses of the individual isotopes,[5] as determined from their mass spectra, the name

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[5] Statement as "Cadmium 110–114" means that all the intervening isotopes have been separately and individually proved to exist.

1	Hydrogen	H	1.008	1	1,008	A		Deviation from 1.000 established; non-isoptopic character demonstrated by Stern-Volmer.
2	Helium	He	4.00	1	4,00	A		
3	Lithium	Li	6.94	2	6,0 7,0	AD	7 » 6	Anode ray method.
4	Beryllium	Be	9.018	1	9,0	Th		Anode rays, parabola method (9.003, 9.001).
5	Boron	B		2	10 11	A		
6	Carbon	C	12.00	1	12	A		
7	Nitrogen	N	14.008	1	14	A		
8	Oxygen	O	16.000	1	16	A		
9	Fluorine	F	19.00	1	19	A		
10	Neon	Ne	20.20	2	20 (21?) 22	A	10 : 1	Isotopy determined by J. J. Thomson by means of parabola method.
11	Sodium	Na	23.00	1	23	AD		Anode rays.
12	Magnesium	Mg	24.32	3	24 25 26	D		Anode rays. A finds only 24.
13	Aluminium	Al	27.1	1	27	A		Result very remarkable, since Al = 27.1.
14	Silicon	Si	28.3	3	28 29 30	A		
15	Phosphorus	P	31.04	1	31	A		
16	Sulphur	S	32.07	1	32	A		
17	Chlorine	Cl	35.46	2	35 37	A		
18	Argon	Ar	39.9	2	36 40	A		Argon 40 and Ca 40 alike within 0.1 per cent.
19	Potassium	K	39.10	2	39 41	DA		Anode rays.
20	Calcium	Ca	40.07	2	40 44	D		Th finds by means of parabola method 39–41 (uncertain). Aston definitely finds only 40. (Anode rays.)
21	Scandium	Sc	45.10	(2)	45 (47?)	A		Anode rays. Result still uncertain.
22	Titanium	Ti	$\left\{\begin{matrix}48.1\\(47.88)\end{matrix}\right\}$	(2)	48 (50?)	A		Anode rays. Atomic weight uncertain.

23	Vanadium.....	V	50.96	1	51	A		Anode rays.
24	Chromium.....	Cr	52.01	1	52	A		Anode rays; somewhat weak.
25	Manganese....	Mn	54.93	1	55	A		Anode rays.
26	Iron..........	Fe	55.84	2	54 56	A	1 : 20	Anode rays and iron carbonyl vapor.
27	Cobalt........	Co	58.97	1	59	A		Anode rays; exactly whole-numbered.
28	Nickel........	Ni	58.68	2	58 60	A	2 : 1	Nickel carbonyl vapor.
29	Copper........	Cu	63.57	2	63 65	A	2,5 : 1	Anode rays; atomic weights exact integers.
30	Zinc..........	Zn	65.37	3	64 66 68 (70?)	D		Anode rays.
31	Gallium.......	Ga	69.72	2	69 71	A		Anode rays.
32	Germanium....	Ge	72.5	3	70 72 74	A	2 : 4 : 5	Anode rays.
33	Arsenic.......	As	74.96	1	75	A		Arsine.
34	Selenium......	Se	79.2	6	{74, 76, 77, 78, 80, 82}	A		Selenium hydride.
35	Bromine......	Br	79.92	2	79 81	A		Methyl bromide.
36	Krypton......	Kr	82.92	6	78 80 82—84 86	A	{84, 86, 82, 83, 80, 78}	Intensity data relative; order of isotopes according to their number.
37	Rubidium.....	Rb	85.45	2	85 87	A		
38	Strontium.....	Sr	87.63	1	86 88	A	3,5 : 100	Absolute value 87.8 (not 88.0).
39	Yttrium.......	Y	88.9	1	89	A		
40	Zirconium.....	Zr	90.6	3 (4)	90 92 94 (96)	A	10 : 2 : 4 : (1)	Atomic weight 91.2 (91.4) does not agree with 90.6; result uncertain.
41	Niobium	Nb	93.5	?		A		Experiments without result.
42	Molybdenum..	Mo	96.0	?		A		Experiments without result.
43	—							
44	Ruthenium....	Ru	101.7					
45	Rhodium......	Rh	102.9					
46	Palladium.....	Pd	106.7					
47	Silver.........	Ag	107.88	2	107 109	A	$J_{107} > J_{109}$	Anode rays.
48	Cadmium.....	Cd	112.4	6	110 114 116	A	4 : 2 : 5 : 3 : 6 : 1	Cadmium fluoride, spectrum same as tin.

49	Indium	In	114.8					
50	Tin	Sn	118.7	8	116—122 124	A		$Sn(CH_3)_4$, spectrum same as cadmium.
51	Antimony	Sb	120.2	2	121 123	A		A: Stibine experiments failed, $Sb(CH_3)_4$.
52	Tellurium	Te	127.5	3	126 128 130	A	1 : 2 : 2	1. Metal. 2. Fluoride; atomic weight 127.5 not understandable.
53	Iodine	I	126.92	1	127	A		
54	Xenon	Xe	130.2	9	{124, 126, 128—132, 134, 136}	A		
55	Caesium	Cs	132.81	1	133	A		Does not agree with atomic weight.
56	Barium	Ba	137.37	1 (3)	(136) (137) 138	A		138 is so intensive that atomic weight is not intelligible even if 136 and 137 are real. Mass recently determined with accuracy as 137.8 (instead of 138.0).
57	Lanthanum	La	139.0	1	139	A		
58	Cerium	Ce	140.25					
59	Praseodymium	Pr	140.6	1	141	A		Not quite definite.
60	Neodymium	Nd	144.3	?	(142—150)	A		Non-resolvable band.
61	—							
62	Samarium	Sm	150.4					
63	—		152.0					
64	—		157.3					
65	—		159.2					
66	Dysprosium	Ds	162.5					
67	Holmium	Ho	163.5					
68	Erbium	Er	167.7					
69	—							
70	—							
71	—							
72	Hafnium	Hf						
73	Tantalum	Ta	181.5					

74	Tungsten......	W	184.0					
75	—							
76	Osmium.......	Os	190.9					
77	Iridium.......	Ir	193.1					
78	Platinum......	Pt	195.2					
79	Gold.........	Au	197.2					
80	Mercury......	Hg	200.6	(6)	(197—200), 202, 204	A		197—200 not separated.
81	Thallium......	Tl	204.0					
82	Lead.........	Pb	207.2					
83	Bismuth......	Bi	290.0	1	209,0	A		
84	Polonium.....	Po	210.0		Radioactive Isotope.			
85	—							
86	Niton........	Nt						
87	—							
88	Radium.......	Ra						
89	Actinium.....	Ac						
90	Thorium......	Th						
91	—							
92	Uranium....	U	238.2					

of the observer (Aston, Dempster, Thomson), the intensity of the positive ray, i.e., the respective "mass proportions" of the isotopes as far as data of more or less exactitude permit, and finally a few remarks of special interest about the methods of investigation, the "form" in which the element was studied and other notable data, e.g., the deviation of a given isotopic mass from whole number, etc.

The concept of "chemical element" has experienced considerable alteration because of the discovery of the phenomenon of isotopy. As a consequence much discussion has been occasioned by the quest for the best possible definition of a chemical element. Fajans insists on the atomic weight as a criterion for such a definition. Chlorine, therefore, with an atomic weight of 35 is an entirely different chemical element from chlorine of atomic weight 37. According to this conception each newly discovered isotope would be a new element. In contrast to this, we have the opinion first expressed by F. Paneth, an opinion which we endorse. Paneth suggests that, as far as chemistry is concerned, it is only the combining weight of the isotopic element that need be considered since the isotopic components are ever present in nature in fixed and constant proportions in the several "mixed" elements. A chemical element may thus be defined as a substance whose several components possess the same nuclear charge; in other words, a mixture of atomic types all endowed with equal nuclear charges. On this basis there would be as many elements as there are atomic numbers. A further distinction—chemically of no merit—may be made by differentiating between a "pure" element and a "mixed" element.

Attention has already been directed to the limitations of modern chemical knowledge and the subsequent impossibility of separating isotopic elements or of discovering differences in their chemical deportment by our present day chemical methods. This is readily intelligible from a physical viewpoint, since the electronic shells of atoms containing the same nuclear charge are entirely similar.

We may now inquire whether there are any appropriate physical phenomena which depend solely upon the mass of the atom. Three such phenomena may be specified, of which two adapt themselves readily to the separation of the isotopic components of a "mixed" element. The third is of great import theoretically, although confirmed in but few instances and in fact theoretically comprehensible in but one case. This third case is that of the spectral emissions of isotopic elements. Are the line spectra of isotopic elements identical? To this query we may respond that the similarity, to say the least, is most striking and marked indeed, not only regarding their optical spectra but for the Roentgen spectra as well, as was demonstrated by Siegbahn and Stensson in the case of lead and its isotopic analogue, Radium G. This similarity in optical spectra conforms to the similarity of chemical character and shows, therefore, that an equal number of electrons are similarly arranged in each of the isotopic elements as to form systems of almost identical configurations.

But nevertheless a *perfect* similarity in line spectra is wanting, a slight difference being expected due to the minimal influence exerted upon the spectra by the mass of the nucleus. Undoubtedly it is of prime importance that conclusive evidence be obtained regarding this influence, so that this problem may be definitely clarified. To date, differences in wave-lengths from isotopic elements have been determined with certainty only in very few instances. Even in the apparently most definite instance—the spectrum of neon, whose isotopes are distinguished by a marked percentage difference—F. Paschen found no conclusive indications, of the isotopy of neon.

It may be noted here that our present knowledge of X-ray spectra does not indicate any evidences of isotopy, i.e., of different nuclear masses.

Lead (which may be grouped with radioactive isotopes) has been subjected to rather extensive investigations which indicate unmistakably that slight differences are discernible for specimens of lead of varying atomic weights. A list of the most important investigations of this phase is appended.

Bibliography of the Investigations of the Line Spectra

(*A*) *Lead Isotopes*

(1) W. R. Harkins and L. Aronberg (J. A. C. S. **42**, 1328, 1920).

A comparative study of the wave-length for the line $\lambda = 4058$ Å. emitted by ordinary lead and by radioactive lead of atomic weight 206.318. Employed the high resolving power of a Michelson 10-inch grating with a 30-ft. Littrow mounting in the sixth order.

The wave-length of line $\lambda = 4058$ Å. obtained from the radioactive lead was 0.0044 Å. greater than that obtained from ordinary lead.

(2) T. R. Merton, Nature, **104**, 93, 406 (1919) (also Proc. Roy. Soc. Lon. **96A,** 388, 1920).

Investigated the lead line $\lambda = 4058$ Å. obtained in the spectrum of ordinary lead, of lead from pitchblende and of lead from thorite (Ceylon). The following results were obtained.

Wave-length of ordinary lead	Wave-length of radioactive lead from pitchblende	Wave-length of lead from thorite
$\lambda = 4058$ Å.	$\lambda + 0.0050$ Å.	$\lambda + 0.0022$ Å.

Degree of accuracy in these observations was ± 0.0007 Å. (These results corroborate the work of Harkins and Aronberg. This is especially so since Merton used a totally different optical system, a Fabry and Perot etalon.)

Merton also examined the thallium line $\lambda = 5356$ Å. Here again the radioactive substance yielded a greater value for the specified line.

Wave-length of ordinary thallium	Wave-length of thallium from pitchblende
$\lambda = 5356$ Å.	$\lambda - 0.0055$ Å.

These measurements are not so definite as those for lead, the same degree of accuracy not being claimed.

(3) T. R. Merton, Proc. Roy. Soc. Lon. **100**, 84, 1921.

This is practically a continuation of the previous research. A number of lines produced in the spectra of lead of various sources were investigated.

Wave-length of ordinary lead of various sources	Wave-length of lead from Australian carnalite	Wave-length of lead from Joachimstal pitchblende
$\lambda = 4058$ Å.	$\lambda = 4058$ Å.	$\lambda = 4058$ Å.
	Diff. 0.011 ± 0.0008 Å.	Diff. 0.005 ± 0.0007 Å.

The differences observed for the several samples of ordinary lead in all cases were smaller than 0.001 Å.

Using Australian carnalite, Merton also investigated the lines listed below. In each case a difference was observable.

λ 3740	3680	3640	3573
$\Delta\lambda$ 0.0074	0.0048	0.0070	0.0048

A difference in wave-length is thus demonstrated. It should be noted, however, that the observed differences are greater[6] than those predicted on the basis of certain simple assumptions.

[6] The difference obtained by Merton is about 200 times more than that predicted on Bohr's theory for a hydrogen-like atom; but the discrepancy carries no significance as applied to lead atoms. Tr.

Nevertheless this observed difference seems to be real since L. Aronberg (Astrophysical Journal, 27, 1918) noted similar results. On the other hand, the spectra of the thorium isotopes showed no such differences.

(*B*) *Lithium Isotopes*

(4) J. C. McLennon and D. S. Ainslie, Proc. Roy. Soc. Lon. 101A, 342, 1922.

These investigators examined the red line of lithium $\lambda = 6708$ Å., which is a very narrow double line analogous to the other alkalis. The source of light was a lithium arc in a vacuum chamber. The high resolving power afforded by a Lummer plate and a 30-plate echelon grating crossed with a Lummer plate revealed the specified line as composed of four (4) lines or two (2) narrow doublets, of which one belongs to Li = 6 and the other to Li = 7. A definite assignment of these four lines to lithium 6 and 7, as characteristic of the two isotopes, was not possible without serious theoretical difficulty. In spite of this, however, it may be contended, with reason, that the quadruple character of the line be ascribed to the isotopy of the lithium atom.

The theoretical inquiry into the influence of the nuclear mass upon the emission of line spectra consists largely in its relation to the Rydberg Number. At any rate, we may present here the formula expressing the anticipated variations in wave-lengths for two isotopes of masses A_1 and A_2 respectively, viz.:

$$\Delta\lambda = \frac{\mu}{m}\left(\frac{1}{A_2} - \frac{1}{A_1}\right)\lambda,$$

wherein μ is the mass of the electron, and A_1 and A_2 the "atomic weights." In the case of chlorine, for example, a doublet of wave-length difference $\Delta\lambda$ of about 10^{-6} would be expected,[7] since the ratio $\mu/m = 5.5 \times 10^{-4}$ and $\left(\frac{1}{A_2} - \frac{1}{A_1}\right)$ is of the order 10^{-3}. That is, chlorine (35) should have a wave-length greater by this amount than that of chlorine (37). For heavier elements, this wave-length difference is still smaller. For infra-red neon lines of 8000 Å., $\Delta\lambda$ should be about 2×10^{-2} Å.

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[7] Too small to be observed experimentally. Kratzer, Z. Physik, 3, 460, 1920.

As stated above, such doublets were not observed by Paschen. Apparently the simple formula is not applicable to the "higher" atoms, i.e., those with more than one electron.

Isotopy and Band Spectra

This problem may be solved, perhaps, when suitable amounts of homogeneous isotopes are made available for experimentation. The minuteness in the wave-length differences of these line spectra of isotopes may be attributed to the fact that one of the vibrating particles involved in the spectrum production is the electron, whose mass, although not negligible, is so small, compared with the nuclear mass. A more marked influence of mass may be looked for, however, in certain band spectra of isotopes, largely because in them the effect of mass vibration is more directly observable. A. Kratzer [8] and F. W. Loomis have attempted, almost simultaneously, to find in the infra-red spectrum of the vapors of their respective hydrogen halides a spectroscopic confirmation of the isotopy of chlorine and of bromine. Here the vibrating system would be comprised of two nuclei, and not one nucleus and one electron. In the theory of band spectra, an essential rôle is played by the energy of the several nuclei vibrating relative to one another within the molecule. In the expression for this energy there occur in the first place electric forces independent of the mass; and in the second place, the "reduced" mass "M," composed of the masses of the vibrating components of the molecule, according to the equation [9]

$$1/M = (1/m_1 + 1/m_2).$$

Since this energy, in some way, affects the frequency of the emitted lines, different frequencies (doublets) are to be expected in vapors, as for example in hydrogen chloride vapor, in which molecules of various types are present, viz.:

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[8] The following is taken from A. Kratzer, Zeitschr. f. Phy. 3, 460 (1920).

[9] This formula would be $(nh/2\pi)(\sqrt{k/M})$, where k is constant, depending only on electric attraction, and m is the resultant or reduced mass. Kratzer, C. A., 1452, 1921.

molecules of the type HCl_{35} and molecules of the type HCl_{37}, due to the isotopy of chlorine. In point of fact, the vibration difference of the resulting lines for these two molecular types is found to be numerically

$$\Delta_{HCl} = \frac{\nu}{2}\left(\frac{1}{35} - \frac{1}{37}\right) = 0.77 \times 10^{-3}\nu.$$

There must be combined with this expression, showing the effect of mass upon nuclear vibration, the consideration of the rotation frequency of the atom, since here again the moment of inertia, i.e., the mass, is an important factor. Calculations, however, produce values for $\Delta\nu$ of such small magnitude whose measurement becomes impracticable. We shall, therefore, confine ourselves and indicate the calculated influence of nuclear vibrations upon the infra-red spectrum of hydrogen chloride as obtained from the data of Imes.[10] These should be so manifest as to exhibit each line as a doublet; in other words, each line should be attended by a satellite. Furthermore the intensity of the two components must be in the same proportion as are the relative amounts of Cl_{35} to Cl_{37} in the isotopic mixture. The fundamental vibration frequency of hydrogen chloride, calculated theoretically, is $\nu = 2877$ cm.$^{-1}$; that is to say, the vibration difference, according to $.77 \times 10^{-3}\nu$ (as given above), is 2.21 cm.$^{-1}$; for the "octave" higher, $\nu = 5657$, while the corresponding $\Delta\nu = 4.36$ cm.$^{-1}$ or, expressed as wave-lengths, 13.5 A. The measurements of Imes indicate clearly the presence of this doublet for the "octave" vibration. Figure 6 shows graphically the measurements of the infra-red band of the hydrogen chloride spectrum. It is evident that each line is accompanied by a satellite (on the long-waved side) which is attributable to the presence of

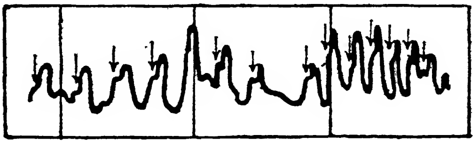

Fig. 6.

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[10] Imes, Astrophysical Journ. 50, 251 (1919).

HCl_{37} molecules. Calculations based upon these data show a difference of 14 Å. as opposed to the value 13.5 Å. required by theory. In view of the experimental accuracy attainable, this is indeed a remarkable agreement. The resolving power of Imes' grating is too small to indicate a corresponding duplicity in as definite a manner for the principal band. Nevertheless, the noticeable width of the lines suggests that doublets are likewise present in it.

The spectroscopic evidence of the isotopy of chlorine was thus established and simultaneously a reasonable guarantee of the correctness of our notions concerning the production of infra-red band frequencies of heteropolar compounds was indicated.

Spectroscopic analysis of band spectra of isotopic elements can likewise prove serviceable in establishing the existence of isotopes where such existence is doubtful and more or less uncertain according to Aston's method. Thus, Aston's method failed to indicate definitely the existence of Si_{29}, in addition to Si_{28} and Si_{30}, because particles of SiH and of SiH_2 continuously appeared in the positive rays in addition to Si. Obviously Si_{29} and $Si_{28}H$ (molecular weight $= 28 + 1 = 29$) may very easily be confused and mistaken for one another. Mulliken[11] has shown, however, that analysis of the band spectrum of silicon nitride demands of necessity the existence of silicon atoms of mass = 29, even though they were present in rather minute quantities. This interpretation of band spectra receives further convincing corroboration in the subsequent discovery by Mulliken of the isotopes Cu_{63} and Cu_{65} (probably CuH).[12] Other band spectra investigated by Mulliken are those of boron oxide and boron nitride.

The Separation of Isotopes

We will now concentrate our attention upon the problem of isotope separation. Chemical methods fail utterly. The

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[11] Mulliken, Phys. Rev. 25, 119, 1925.

[12] Mecke and Frerichs (Bonn) likewise attribute the doublet-structure of CuH bands to isotopy-effects of copper.

Method of Aston to prove the phenomenon of isotopy, by its very nature, brings about such a separation. But this method does not lend itself easily to the production of isotopes in considerable quantities. The production and eventual availability of larger quantities of the "pure" element is a problem of great scientific significance; for it is important to know just how the behavior of several elements possessing similar nuclear charges depends upon the mass of the nucleus. Further, how does this nuclear mass affect the nature of their respective spectral emissions—to which we have already alluded—their electrical conductivity and their specific heats; and finally are the chemical reactions of such elements similar "in toto"?

It was mentioned elsewhere that there are certain physico-chemical processes which, cæteris paribus, depend solely upon atomic mass. Suggested methods to accomplish isotopic separation are evaporation at very low pressure, separation by thermal diffusion, by mass diffusion, etc. We shall outline briefly the principles of three methods to separate isotopes, viz.: the method of Hevesy and Brönsted, the method of Stern and Volmer and lastly the method of G. Hertz. These three processes are based, in principle, upon the fact that atomic speeds depend upon atomic mass.

Assume a liquid to be a mixture of two isotopes of mass m_1 and m_2 respectively; eventually, the vapor standing above such a liquid will possess the same composition as the liquid due to the equal vapor pressures of the isotopic components. To be sure, the lighter atoms of mass m_1 will leave the liquid surface to enter the vapor phase with a greater velocity than do the atoms of the greater mass m_2. Indeed the velocity v is greater by the ratio $\sqrt{m_2/m_1}$. Consequently $\sqrt{m_2/m_1}$ times as many atoms of the lighter variety will enter in unit time into the gas phase. It must be remembered, however, that the reversal of this phenomenon will proceed in a similar and proportionate manner until equilibrium conditions are established; for, simultaneous with this phenomenon of the more rapid vaporization of the lighter isotope, there is in marked evidence a more rapid condensation of its vapor than of the heavier component. It is of the utmost importance, therefore, when separating isotopes by vaporization methods, to eliminate the possibility of condensation and to avoid the establishment of equilibrium conditions. These experimental procedures, together with requisite precautions, were attained by Hevesy and Brönsted by vaporizing the isotopic mixture in vacuo under low vapor pressure so that these molecules which pierce the surface of the confined liquid will be condensed immediately upon a cooled object conveniently placed near the vaporizing liquid. By this means all collisions of atoms present in the vapor phase may be avoided or reduced to a minimum. Obviously a high vacuum and a moderate (not too high) vapor pressure are requisite conditions for the success of such procedure. As a result "back" condensation is avoided to a considerable extent, thereby permitting a more or less complete separation of m_1 and m_2 because of the more efficient utilization of their respective vapor speeds. In an ideal case the respective isotopes should be found upon the cooled surface in the proportions $\sqrt{m_2}/\sqrt{m_1}$, i.e., the lighter. isotope should be present in the condensate with a concentration $\sqrt{m_2}/\sqrt{m_1}$ times its concentration in the vaporizing liquid. The condensate will thus possess a lower average atomic weight than will the residue. This condensate may now be subjected to a series of fractional distillations whereby a further concentration of the isotopes is obtained in each successive condensate.

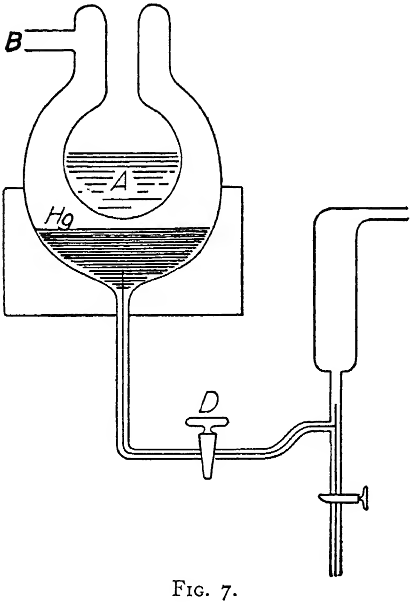

Fig. 7.

Figure 7 presents a diagrammatic sketch of the apparatus employed by Hevesy and Brönsted to affect the isotopic separation of mercury. The larger vessel contains sufficient mercury, Hg, so that its surface is distant about 1–2 cm. from the vessel *A* which is cooled by means of liquid air contained within it. The side outlet tube *B* leads to an efficient vacuum pump. The vessel was placed in a temperature bath heated to 40° C.–60° C. After an appropriate time interval to permit vaporization of the mercury isotopes the residual mercury was removed by way of cock *D*. Upon the subsequent evaporation of the liquid air contained in *A*, any mercury vapor that may have condensed during this interval upon the outer wall of *A* is shaken off and finally drained in the same manner as was the residual mercury. This process is repeated with fresh mercury until several liters (27) have been so fractionated. The specific gravities of the condensate and of the residue are then determined with great accuracy. The residual (unvaporized) mercury was then substituted for the normal mercury in Hg, and in turn likewise partially vaporized, so that the resulting second residue yields a greater concentration of the heavier isotope. This process is repeated several times so that each succeeding residue becomes richer in the heavier isotope. The condensate, in turn, is then subjected to a similar fractionation process, whereby a lighter isotope is obtained. In each case the condensate is transferred from the condensing surface *A* to Hg and the residual mercury drawn off through *D*. The final condensate yields a product rich in the lighter isotopic component. The data of the appended table illustrates the variation in specific gravity after repeated fractionations. R_n designates the residue and D_n the condensate after the *n*th fractionation. The specific gravity of ordinary mercury is taken as 1.000000.

The maximum difference obtained for each set of fractions is about .025 per cent while the difference between the heaviest and the lightest fraction amounted to .05 per cent. Differences in the electric constants of the various isotopic mixtures were not discernible.

Fraction	Specific Gravity	Fraction	Specific Gravity
R_2	1.000016	D_2	0.999953
R_4	24	D_3	33
R_{12}	79	D_4	11
R_{14}	1.000134	D_5	0.999881
R_{18}	23	D_{14}	74

This method is not applicable to solid bodies inasmuch as its successful utilization prescribes that the surface of the vaporizing substance should not consist only of the heavier component after the lighter one has evaporated from it. Calculations will show, in case of mercury, that the "self-diffusion," which is a measure of the mixture within mercury, is so extensive that with an approximately slow evaporation (not more than 5×10^{-3} c.cm. per surface unit per second) a sufficient intermixing of the components results.

The method adopted by Stern and Volmer is based upon the dependence of diffusion rates upon the mass of the diffusing substance. Two gases of mass m_1 and m_2, respectively ($m_1 < m_2$), diffuse through a membrane in the proportion $\sqrt{m_2}/\sqrt{m_1}$, the lighter gas moving faster than the heavier. If, therefore, a gaseous isotopic element is permitted to flow along a porous porcelain tube, the lighter component will diffuse through the wall to a greater extent than will the heavier and consequently will increase in concentration on the outside while the heavier component will diffuse less rapidly, thus increasing its concentration only on the inside. The immediate purpose of the problem, as investigated by Stern and Volmer, was an attempt to determine whether or not hydrogen is a mixture of isotopes, a question whose solution has a significant bearing upon many other interesting and important phases of the subject matter. It may help explain the deviation of the atomic weight of hydrogen from unity; it may clarify the unsolved and perplexing problem regarding the existence of an element (or elements) whose atomic mass lies between that of hydrogen and helium;

finally, the discovery of the existence of such an isotope of hydrogen would supply an experimental basis for consideration and speculation regarding the structure of atomic nuclei.

The experimental procedure finally adopted by these investigators was somewhat as follows. Several hundred liters of hydrogen were allowed to stream through a clay tube which was surrounded by an envelope of water vapor so that the hydrogen diffused outward and the water vapor inward. The latter acted as a diluent and as a "stirrer" since its diffusion in a direction opposite to that of the hydrogen causes sufficient mixing of the diffusing components. Without this serviceable action on the part of the water vapor, the heavier hydrogen components (if there be any) would form rapidly in such large concentrations on the surface of the clay tube after the diffusion of the lighter component that even after a short time the diffusion process no longer could fulfill its task of separating the components. Reference has already been made to a similar difficulty experienced in the vaporization of liquid or solid surfaces.

Since the purpose of this investigation was the demonstration and eventual isolation of the isotopes of hydrogen, Stern and Vollmer tested their apparatus with a mixture of hydrogen and oxygen. These tests having proved satisfactory, they diffused several hundred liters of hydrogen and burned to water the undiffused hydrogen—which should contain any heavier component in greater concentration—remaining within the tube, the resulting water vapor being continuously removed from the inside of the tube by condensation. The specific gravity of this water was then determined and subsequently compared with that of ordinary water. Absolutely no difference was detectable in the specific gravity of water made from normal hydrogen and that produced from the hydrogen fractionated by this diffusion process. On the assumption that the difference of 0.008 over 1.000 in the atomic weight of hydrogen is attributable to the existence of a heavier isotopic component in ordinary hydrogen, the specific gravity of this water should be greater than the normal by 4.2×10^{-2} per cent, whereas the observed deviation proved to be only 6×10^{-5}.[13]

Using the same method, oxygen was also proven to be non-isotopic in structure.[14]

These researches without a doubt have produced unfailing evidence of the non-isotopic structure of the substance hydrogen; furthermore, the method, as outlined, was adopted particularly in America and utilized on a large scale for many isotopic separations, especially in the case of chlorine. No startling or unlooked-for results however have to date been obtained. Harkins obtained fractions of HCl which differed from one another by 1/500 of their molecular weights.

A novel procedure for the separation of gas mixtures was devised recently by G. Hertz,[15] although its applicability to isotope separation has not yet been tested. Its characteristic feature is the utilization of a stationary diffusion process in a streaming gas. The gaseous mixture to be separated is admitted into a tube in which a vapor is flowing and is allowed to diffuse into this vapor as the latter streams against the mixture. For this purpose an easily condensable vapor is chosen to prevent the removal of the gaseous mixture. The lighter component diffuses more rapidly against the stream of vapor than does the heavier component and their subsequent separation will be more complete the longer the gaseous mixtures stream against the vapor. Theoretically the lighter gas should be obtained in an almost pure state. Using this diffusion method, Hertz obtained spectroscopically pure Helium by separating a mixture of 30 per cent helium and 70 per cent neon. Not the faintest spectroscopic evidence of neon was detectable in the helium fraction. Next to the method of Brönsted and Hevesy for fluids, this is the best known method applicable to gases.

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[13] In other words, the calculated deviation from the normal density is 700 times the observed deviation. Tr.

[14] In this instance the calculated deviation proved 180 times the observed. Tr.

[15] G. Hertz, Physik. Zeitschr. 23, 433 (1922).

Transition of Isobars. Transmutation of Elements

As an appropriate conclusion to our considerations regarding the isotopy of elements, it remains for us to draw attention to the recent experiments of Miethe and Stammreich and of Nagaoka upon the transition of elemental mercury into gold. Such a change should take place whenever mercury atoms are bombarded by electrons, a condition prevailing in discharge tubes filled with mercury vapor, in the mercury vapor lamp and in other similar discharges between mercury electrodes. It was found experimentally that the mercury employed always gave evidences of the presence of gold, although previous to the experiment it had been shown to be "gold free" by its failure to respond to the same analytic procedure. In the meantime, however, many comprehensive control experiments were carried out, notably by Haber and Tiede, which indicate without a doubt that Miethe's results do not warrant the conclusion of the possibility of such a transition of elements. The chemical and physical evidences of gold have been made by sensitive tests by Haber. There is no longer any doubt, therefore, that the traces of gold found by Miethe were partly present originally in the mercury and partly admixed in some unknown manner during the electrical manipulations and subsequently during analysis. It is necessary, therefore, that further experimental work be carried out, before the mechanism of such a transmutation be considered from a theoretical point of view. We will stress but two points here as regards the isotopy of these two elements. Gold and mercury are distinguished by a difference of one unit in their respective atomic numbers, i.e., in the positive electric charges. Both gold and mercury are isotopic and individual mercury isotopes doubtless are isobaric with those of gold; for gold must yield isotopes of mass greater than 197 and mercury has isotopes ranging from 197 to 200.

To change mercury into gold, therefore, it is necessary to introduce an electron into the nucleus of a mercury atom.

In this wise, the mass remains constant while a positive nuclear charge of the mercury becomes neutralized, whereby its atomic number decreases by one unit. In other words, it becomes equal to that of gold. But, as already stated above: we must await further experimentation and for the moment such an elemental transmutation must not be regarded as an "a priori impossibility."

CHAPTER III

ATOMIC RAYS AND SOME ATOMIC PROBLEMS SOLVED BY THEIR MEANS

The condition of equilibrium of a liquid in contact with its vapor is characterized by the fact that in unit time as many molecules leave the liquid phase to enter the vapor phase as vapor molecules condense upon the surface of the liquid. Such a condensation of vapor particles is likewise present during the volatilization of solid bodies. The only requisite for this phenomenon is the establishment and the maintenance of a constant temperature throughout the entire system, i.e., the vessel in which is contained the liquid or solid body in contact with its vapor. As soon as this condition fails to prevail, a decidedly different procedure, accompanied by a disturbance of equilibrium, sets in; thus distillation or sublimation may take place. Under such conditions not all the vapor molecules return to the liquid or solid phase, some being condensed at points of such lower temperature at which the vapor pressure is lower than at all other points within the system. Eventual restoration of equilibrium will result only when the entire substance has reached this point of lowest temperature, whereupon the vapor pressure corresponding to this temperature will prevail throughout the entire system. If it is desired further to minimize vaporization, it will be necessary to provide some means whereby, as a result of molecular collisions, as many as possible of the vaporized molecules find their return path to the liquid or solid phase. Application of this principle obtains in the construction of incandescent lamps. A metallic element tungsten (or platinum) subjected in a vacuum to a sufficiently high temperature slowly evaporates. Thus the volatilization of a highly heated tungsten filament is evidenced by the black film upon the glass of lamps that have been in service for an appreciable time. Suppose, however, that the lamps are filled with an indifferent gas, rather than being highly evacuated. Because of the greater molecular concentration, the vaporized metallic tungsten atoms now will rebound very frequently from the gaseous particles in the immediate neighborhood of the glowing filament, whereby their greater number are reflected back to the filament. In other words, the "back diffusion" of the vaporous tungsten has decidedly increased. Naturally, this phenomenon takes place at the expense of electrical energy, since there is produced, due to the gas now present in the previously vacuized vessel, a higher thermal conductivity, whose amount must be compensated for by the stronger heating of the filament, if the lamp is expected to burn with a luminosity (equal temperature) equal to that of the highly evacuated lamp.

When, however, the incandescent lamp is highly evacuated (let us say the pressure within the vessel so diminished that the free path of the remaining gas molecules is large in comparison with the dimension of the lamp), then the atoms vaporized from the filament surface will continue their rectilinear motion until they impinge upon the glass wall and are condensed upon it; i.e., a deposit is produced. If an obstacle, e.g., a filament support, be situated between the vaporization filament and the glass wall, some of the atoms will deposit upon it, i.e., not all atoms will reach the wall. As a result a "shadow" is produced. In other words a "bright" section appears in the otherwise equally darkened deposit upon the wall. This observation (of W. A. Anthony) embodies the intrinsic characteristic of the phenomenon to which has been given the name of "atomic rays," viz.: atoms.

The existence of atomic rays was soon forgotten but after a long period of neglect they were rediscovered by L. Dunoyer in 1911. Only since 1919, however, have atomic ray investigations begun to attract attention and assume a prominent place of interest. This is due largely to the work of O. Stern and M. Born.

It will not be amiss to consider at this point the possibility of utilizing these rays for the solution of certain physical problems. It is evident, without further discussion, that they are especially suitable for the investigation of atomic phenomena. It is, however, not so much the individual atom, but rather a collection of several atoms, each of which moves in a beam entirely independent of the other, that permits study and investigation of their respective speeds, their relative deflections from the rectilinear path after collisions, and finally their reaction towards forces (as gravitational, magnetic or electric) impressed upon them. Furthermore, although the individual atom is so small as not to fall within the range of visibility, nevertheless it can be intercepted and made to deposit, after its passage through one of the specified fields of force, upon a conveniently placed plate and so contribute to the formation of visible layers by the accumulation of the deposits of the individual atoms. A comparative study of the respective deviations experienced by these atoms and by other atoms not subjected to the influence of a specified field of force is hereby made possible. However, for such a comparison to be of value, it is requisite that all atoms impinging upon the plate firmly adhere to it and not revaporize from it. Such a quantitative condensation of the vaporous substance invariably occurs when the temperature of the "receiving" plate is very low as compared to the melting point temperature of the substance; for metallic vapors, for example, this may be accomplished very effectively by cooling the plate with liquid air. M. Knudsen and R. W. Wood have established definitely that each substance is characterized by a definite critical temperature below which its gaseous particles are condensed completely upon the receiving plate. Further investigations of this phase of the subject have been, and still are, in progress, but with no definite and obvious results. It should be emphasized also that this critical temperature is characteristic not only of the substance producing the rays, but of the material of the receiving plate as well.

Knudsen[1] thoroughly examined the condensation and

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[1] M. Knudsen, Ann. d. Phys. 50, 472 (1916).

reflection (re-vaporization) respectively taking place on well-cleaned glass surfaces. The following temperatures were observed below which neither molecules nor atoms of the specified substance are reflected any longer from the surface, but all remain completely condensed upon the plate as a firmly adhering deposit or film on their first impact. Above this temperature condensation does not take place.

	Critical Temperature	Melting Point	Boiling Point
Ammonium chloride	$<-183°$		
Mercury	-140 to -130	-38.9	357
Zinc	Between -183 and -78	419.4	920
Cadmium		321	770
Magnesium		630	~ 1100
Copper	Between 350 and 575	1084	~ 2100
Silver	Above 575	961	?

It is apparent, as indicated by the data of this table, that there exists no simple relation of the critical temperature of the several substances investigated to their respective melting points or boiling points. The influence of the material constituting the reflecting surface is shown in an experiment performed by Knudsen, in which it was observed that mercury surfaces, whether solid or liquid, firmly hold every impinging mercury atom. A similar phenomenon may obtain for other substances according to Langmuir. It is very appropriate at this point to make reference to the very interesting work of J. Weyssenhoff[2] who has added considerable experimental material to this question as applied to the condensation of atomic mercury rays upon gold surfaces and their reflection, i.e., their eventual re-vaporization from such surfaces. The data of the above table indicates in addition that there are a number of substances which are

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[2] H. V. Weyssenhoff, Ann. d. Phys. 58, 505 (1919). (Weyssenhoff found a decided difference between gold and iron as regards their reflecting power; but mercury condensed upon gold surfaces would stop the reflection of further mercury molecules. Weyssenhoff hopes to demonstrate eventually whether or not any reflection takes place at all from gold surfaces. (C. A., 1919, 2789.) Tr.)

condensed quantitatively upon plates at room temperature. Typical among these are the metals copper, silver and gold, but not the metal zinc. Sodium clings and adheres to glass to a rather remarkable extent at room temperature. When an atom is reflected—one may say that the previously condensed atom after a brief stay upon the condensing surface undergoes a second vaporization—it speeds back and forth between the fixed walls, thousand of times, until finally it has lost so much of its initial velocity that at a subsequent impingement upon a solid it will remain firmly attached thereon.

This problem of the reflection of atoms from solid surfaces may be of special interest to, and perhaps may throw some helpful light upon, the still unexplained and perplexing phenomenon of the absorption of vaporous molecules upon solid surfaces.

These, however, are by no means the only influences that have a decisive bearing on the question of condensation and reflection (better expressed as re-vaporization, since reflection in the optical sense does not take place at all or, at best, to a very minimal extent). Inquiry into these factors suggests the possibility of formulating a picture of the manner of formation, i.e., the genesis, of these deposits. Precisely as in the theories of crystal growth, this "picture" is expressible as a nuclear condensation theory. It was observed that, next to the temperature of the "receiving plate," the "radiation density," the extent of the surface "bombarded" by the atoms are of greatest significance. Thus, receiving plates at temperatures considerably above the critical temperature become coated (encrusted) provided the "radiation density" is sufficiently high, i.e., if the impinging particles follow upon one another very rapidly. What is more, the larger the irradiated surface the more rapidly does the deposit form (develop). Both these facts are easily intelligible.[3] After

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[3] For details, see W. Gerlach, "Ergebnisse der Exacten Naturwissenschaften," 3 (1924), article on "Atomic Rays"; also A. C. Cilliers, Diss. (Frankfurt a. M., 1924), and also recent researches of Estermann.

their impact upon the surface the atoms cling fast for a time during which interval they execute a motion of some kind prior to their re-evaporation. Should they meet, during this retention interval, other atoms which have impinged at other points along the surface, firmly placed condensation nuclei will henceforth be developed. The probability of such mutual meeting obviously becomes greater, the denser the radiation and the more extensive the impacted surface.

It becomes necessary, in certain experimental procedures, to utilize beams of rather narrow cross section. These may be procured by inserting very fine slits or diaphragms between the vaporization source and the deposition plate so that only those atoms that pass through the diaphragm openings—that is, all those moving in exactly the same direction and coaxial with the slit—will strike upon the deposition plate. This procedure renders atomic rays parallel much in the same manner that parallel X-ray beams are obtained. Naturally enough, the greater number of atoms will thus be blocked by the diaphragm so that relatively only a few vaporized atoms will ever reach the plate. Furthermore, metallic deposits become optically perceptible only when they have acquired a thickness of 4–7 atomic layers. Such thicknesses are obtained only after long and extended and impracticable vaporizations. It was necessary, therefore, to elaborate a process whereby an optically undetectable layer could be magnified without disturbing or altering the geometric configuration of the deposit. Two processes, designed for such magnification, have been utilized with considerable success in the case of silver, copper, gold, bismuth, tin, antimony, lead and others. The first method is essentially similar to the daguerreotype development process of Kalähne, except that cadmium vapor is substituted for the normally used mercury vapor. If a thin and optically imperceptible layer of one of these metals is placed in an evacuated chamber in which cadmium vapor is being generated, the latter will condense under the proper—obviously very low—vapor pressure only at such points where metallic atoms are already situated.

In other words, it will be precipitated upon the thin deposit produced by the atomic ray particles. From glass surfaces the cadmium vapor is reflected immediately. Apparently this phenomenon is analogous to the clinging of mercury atoms upon mercury surfaces described above. The second method,[4] also applicable to, and tested for, copper, silver, and gold, makes use of the development process employed in the fixation of exposed photographic plates. The atomic ray particles are deposited, as described, upon a plate previously cleaned, in turn, with nitric acid, chromic acid, a 2 per cent solution of hydrofluoric acid and finally with distilled water. This is then placed in a bath in which nascent silver continuously separates out, the latter precipitating or "crystallizing" out upon the metallic atoms already present which serve as nuclei for subsequent deposition. R. E. Liesegang [5] suggests the following formula for the development bath. Two grams of silver nitrate are dissolved in 100 cc. of a 10 per cent gum arabic solution. This solution must be preserved in amber bottles or stored in the dark. In a second 10 per cent gum arabic solution one gram of hydrochinon is dissolved. For "development" of the atomic deposit equal parts of solutions are poured over the plate upon which is deposited the invisible layer. After an interval of $\frac{1}{2}$ minute, finely divided silver very slowly commences to separate out with a progressively increasing speed. The first atoms, so liberated, precipitate themselves upon the atomic layer already adhering to the plate and thus increase the depth of this layer. This development process may be repeated very frequently, but the bath must be renewed as soon as the solution assumes a grayish appearance. When changing the bath and during washing of the plates care must be exercised lest perhaps the silver sludge of the solution imbed itself upon the plate, and thus impair the

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[4] W. Gerlach and O. Stern, Zeitschr. f. Phys. 9, 349, 1923. Stern and Estermann have developed, by this method, deposits of 2×10^{-9} cm. thickness. Experimental data still unpublished (see below).

[5] R. E. Liesegang and W. Rieder, Zeitschr. f. wissensch. Mikroskopie u. für mikroskopische Technik, 38, 334, 1921.

development of the original deposit. It has been found possible by this method to increase layers which are much less than a single atom in thickness to such thicknesses that they will reflect metallically. In development the deposits retain their original geometric configuration.

O. Stern and the author developed deposits according to the following formula. Several cc. of a 1 per cent hydrochinon solution are treated with a few drops of concentrated gum arabic solution; the plate to be developed is immediately brought into the mixture. About 1 cc. of a 1 per cent silver nitrate solution is then added to this liquid. The thinnest layer successfully made visible by this method was 2×10^{-9} cm. thick. By way of comparison this represents 1/10 atomic thickness. This indicates that silver atoms, even when separated by multiples of their diameters, can be "developed" to thick metallic layers.

The crystal structure of silver films, formed by the deposition of atomic particles until their metallic nature was visible, were examined by the author according to the method of Debye and Scherrer. No developing or other magnification process was employed in the study of these films. It was observed that they were a conglomerate of very fine silver crystals grouped with no special orientation. They presented exactly the same appearance as pulverized metallic silver.

We shall consider three problems of a more special character that have been solved by means of atomic rays. The first two deal with the direct measurement of magnitudes which play an important rôle in the kinetic theory of gases; viz.: the direct measurement by Otto Stern of molecular thermal velocities and the determination by Max Born and Elizabeth Bormann of the mean free paths of molecules. The third problem is the experimental confirmation of the magnetic moment of individual atoms, which recently was accomplished by W. Gerlach and O. Stern.

According to the fundamental principles of the kinetic theory of gases the kinetic energy of moving atoms (or molecules) depends only upon their temperature. If m represents the mass, c the mean velocity of the atoms at temperature T abs., and K the Boltzmann constant, then

$$\tfrac{1}{2}mc^2 = \tfrac{3}{2}KT$$

or

$$c = \sqrt{3KT/m}. \qquad (a)$$

If the molecular mass ($= N \times m$) is designated by M and the gas constant R substituted for the Boltzmann constant NK, then obviously (a) becomes

$$c = \sqrt{3RT/M}$$

from which

$$c = 157.9\sqrt{T/M} \text{ meters per second.}$$

Or

$$M = 2.49 \times 10^4 c^2/T.$$

This last equation indicates how the molecular mass of the substance m may be obtained from the observed velocity. The plan adopted by Stern[6] for measuring the mean velocity is similar to the Hartman-Kempf method for determining the velocities of rapidly moving projectiles. Selected particles of atomic rays are projected in a specified direction with a definite mean free path, greater than the length of the containing vessel. After traversing a given distance they strike upon a metallic plate where they condense as a dark line. If the plate is rotated rapidly about the atomic source as axis, the moving atoms no longer strike it at the same points, but will impinge upon it at a specified distance from these points, the condensation lines being displaced by an amount depending upon the velocity of the atomic ray, and the rotation speed of the sensitized plate. This is apparent from the following considerations. Inasmuch as the atomic particles are moving uniformly in a straight line, a specified time proportionate to their velocity will have elapsed between their departure from the source and their eventual impingement upon the plate. During this interval the plate, due to

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[6] O. Stern, Zeitschrift f. Phys. 2, 49 (1920).

its rotation, obviously has altered its position. The localization of these several condensation lines, therefore, depends solely upon the two factors, molecular velocity and relative rotation speed of the plate. Let d designate the distance from the source to the plate and c the molecular velocity; obviously the time t (elapsed before the particle reaches the plate) will be

$$t = d/c;$$

further, if the plate makes n revolutions per second, it will traverse the distance s,

$$s = 2\pi dn,$$

in a second, or in t seconds,

$$s = 2\pi dnt;$$

putting $t = d/c$, this last expression becomes

$$s = 2\pi d^2 n \frac{1}{c},$$

which shows the relation between position of the condensation line and the molecular velocity.

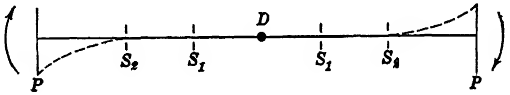

Fig. 8.

Figure 8 represents a diagrammatic sketch which may prove helpful for a better orientation of the method of procedure. In practice, the silver molecules were obtained by the volatilization of a silver filament coated about a platinum wire, D, heated electrically; only those particles were utilized whose paths were directed against the plate P by means of conveniently placed diaphragmatic openings S_1 and S_2. The wire was in line with the axis of the revolving wheel, whose periphery carried the sensitized plate. The number of revolutions of this wheel was $n = 25$ per second. The whole apparatus was confined in a highly vacuized chamber (0.0001 mm. Hg). The dash lines indicate the paths of the silver atoms after passing through the slits while the plate is rotating in the direction specified by the arrow head. With alternate clockwise and counter-clockwise rotation of the plate there were obtained two condensation deposits separated by a distance equal to twice the displacement from the rectilinear condensation line, i.e., the condensation line produced when the plate remains at rest. In this way the distance between deposits was found to vary from 0.7 to 0.8 mm. or s (of the above formula) was about 0.35 to 0.40 mm. The velocity was thus found to be approximately 600 m. per second. This ingenious method proved to be the first direct measurement of thermal molecular velocity.

A second significant problem relative to the kinetic theory of gases, viz.: the direct measurement of the free mean paths of neutral atoms, was solved experimentally with the aid of molecular rays. This experiment was first accomplished successfully by M. Born and E. Bormann.[7] Their method is as follows. A silver ray, formed by the passage of silver vapor through a minute opening, streams into a highly evacuated chamber. The ray is sharply defined and of such outline as is imparted to it by virtue of the size and position of the slits through which it passes. In this respect it is entirely analogous to a light ray. The ray is thus divergent. Assume small glass plates to be placed in its path at different distances from the opening in such a way that they mutually do not "block" one another. Purely because of geometric reasons, the number of silver atoms impinging upon unit area of these plates becomes smaller as the distance from the opening increases. A different condition prevails on the other hand, if the silver ray enters, not into an evacuated chamber but into one in which gas particles are confined. The collisions of the silver atoms with these gaseous molecules already present will cause some of the former to be deflected from their initial straight path, so that an inevitable decrease in the concentration of the silver atoms in the ray takes

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[7] M. Born, Physik. Zeitschr. 21, 578 (1920); Bielz, Diss. (Gottingen, 1924).

place. As a consequence, the intensity of the deposits produced upon the several plates decreases more rapidly than is demanded by the geometric relation that obtains in the former instance. Figure 9 represents a diagrammatic outline of the method utilized in this interesting—but none too simple—experiment. *R* is a quartz vessel; the narrow outlet tube in the bottom contains a little silver, electrically heated by means of the resistance coil *O* wrapped about the tube. The silver vapor thus produced rises through the opening *B* into *R*. To confine the heat (1100° C.–1200° C.) in the tube *O* and prevent its conduction throughout *R*, the lower part of the vessel is set in a cooling bath and packed with solid carbon dioxide. The arrangement of the plates is pictured in diagrams 10*a* and 10*b*. Each one of the four segments (10*b*) rests on one of four brass supports *p*, producing a sort of spiral effect. Looking down upon the plates, they exhibit the appearance shown in 10*a*, and do not overlap.

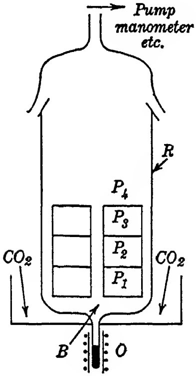

FIG. 9.

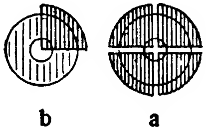

FIG. 10.

To compute the mean free path, it is necessary to measure the thicknesses of the several silver deposits. This is accomplished microphotographically according to a procedure developed in connection with the measurements of Wiener. The silver deposits are iodized and the thickness of the layer determined by means of the interference measurements on the continuous spectrum made between the upper and the lower boundary of the transparent silver iodide films and a plane glass plate. Since the deposits are wedge-form—the plates are not perpendicular to all parts of the beam, again for geometric reasons—the measurements of interference must be limited to small regions of the plates. The iodated silver deposits and the plane glass plates are mounted microscopically and the interference pictures photographed from place to place by means of a spectral-ocular (Zeiss) and a camera. An apparatus specially adapted for this purpose is manufactured by C. Zeiss-Jena according to specifications by M. Born. Computation becomes more or less simple once the thicknesses of the silver deposits are measured. If the thickness for the first plate in a high vacuum is D_{10}, then that for the mean free path will be

$$D_1 = D_{10}e^{-(a_1/\lambda)},$$

where a_1 is the distance of the plate to the opening B. For the other plates, we have, proportionately,

$$D_n = D_{10 \cdot n}e^{-(a_n/\lambda)}.$$

From the values of two plates h and i, we have

$$\lambda = \frac{a_i - a_h}{\log\left(\frac{D_2}{D_1} \cdot \frac{D_{10 \cdot i}}{D_{10 \cdot h}}\right)}.$$

Knowledge of the mean free path permits the further calculation of the sum of the radii of two colliding atoms. Thus, according to the data of Fr. Bielz this sum for silver atoms and nitrogen molecules is 2.58×10^{-8} cm. Adopting the commonly accepted value of the nitrogen molecule radius ($= 1.55 \times 10^{-8}$), the radius of the silver atom becomes 1.0×10^{-8}.

These investigations are still in progress.

The third problem investigated with the aid of atomic rays is the magnetic behavior of individual atoms. This will receive fuller discussion in Chapter VIII.

CHAPTER IV

Molecular Dipoles

Our present knowledge based as it is upon different but closely interwoven experimental evidences unquestionably justifies the conclusion that chemical action as well as the phenomena of crystallization, adhesion and cohesion, adsorption and condensation are all of electric origin; i.e., they are due to electric forces operative within bodies. An electrically neutral molecule may be conceived, indeed, as a more or less complex system comprised of electrically positive and electrically negative charges which quantitatively compensate each other. Such a quantitative compensation, however, does not entail, of necessity, a neutralization of the forces due respectively to the positive and negative electrification, especially when we consider distances of molecular dimensions. To preclude the possibility of such a compensation, evidently it is sufficient that the center of gravity of the electro-positive constituents of a given molecule be not coincident with the center of gravity of its electro-negative constituents. Under such conditions an electric charge in close proximity to a molecule of this type will experience attractive and repellent forces, these being exerted upon it by the molecule's electro-positive and electro-negative constituents; these forces, moreover, will be proportionate to the respective distances of the two centers of gravity to the charge. A molecule characterized by such behavior constitutes a typical electrical dipole; it is termed a "molecular dipole" or briefly a "dipole."

We must distinguish from these natural dipoles such molecules which to all outward appearances are electrically neutral, but which nevertheless may become polarized because of the influence exerted upon them by some exterior electrical force. Such molecules are designated as "induced dipoles"; in them the "inducing" exterior force has occasioned a displacement or shifting of the center of gravity of the positive charges toward that of the negative charges.

An electric field will direct, i.e., orientate, a dipole. This directive force is opposed by the effects of heat motion which is so obstructive and destructive of orientation. The intensity of a given directive force, furthermore, is dependent upon the "strength" of the dipole, which is measured by the "dipole moment" of the molecule, i.e., the product of the distance between the centers of gravity of the positive and negative charges into the magnitude of the charge.

These remarks will become clearer when considered with special reference to a definitely selected case, viz.: the influence, as computed by M. Born, of the dipolar character of a liquid upon the mobility of ions contained in it; as, for example, the ionic mobilities in aqueous solutions. The fundamental premises of these considerations are: a negative ion is an atom carrying a free electric charge; and a water molecule is a natural dipole. The correctness of this latter statement follows from many experimental observations, among them being the behavior of water toward electric waves. The absorption spectrum observed in that spectral region peculiar to electric waves presents evidence of specific vibrations within the molecule, which may be traced back and attributed to the vibrations of oppositely electrified particles within the molecule much in the same manner as are the vibrations of crystals. This will receive fuller treatment in Chapter XXII. A water molecule may, therefore, be pictured as possessing somewhat the following electric character. "*a*" is the distance between the centers of gravity of the positive and negative charges respectively.

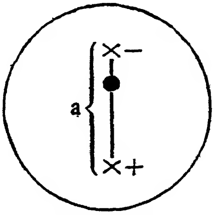

Diagram A

Under normal conditions the "moment axes" of the molecules in liquid water assume all possible positions because of the thermal motion of the molecules. However, if ions are present in the water, those solvent molecules which are situated in the immediate neighborhood of the ions will be influenced electrostatically by them; as a consequence, the water molecules array themselves about the ions fronting against them with that pole which is opposite in sign to the ions, the latter being surrounded completely by a relatively firmly bound shell of water molecules. In other words, the ions have been "hydrated." If now an ion moves or tends to move under the influence of an electric field, its motion is impeded to a greater or lesser extent by definite frictional forces which increase with decreasing ionic radius; this latter phenomenon is due to the fact that water dipoles are "bound" more firmly to the smaller ions because of a greater electrical interaction between ions and solvent molecules. This is Born's explanation of the anomaly arising from the discrepancy in the values of certain ionic mobilities.[1]

The dipole character of a liquid or of a vapor can be demonstrated in several ways. At present no less than four experimental procedures have been elaborated; nevertheless the entire problem itself is still too new, and its relation to other phases of the subject matter too obscure to warrant an exhaustive examination and a critical comparison of these methods and their respective results. One group of these methods investigates the dielectric behavior of molecules, which differs for dipolar and non-polar substances, when they are subjected to the influence of an exterior electric field. This difference arises because the electric field of a natural dipole molecule superimposes itself upon the exterior force. Such influences, therefore, should be discernible plainly in investigations of dielectric constants as functions of temperature. The temperature coefficient of the dielectric constant is conditioned primarily upon the molecular field of the dipole, since this modifies the variations in the dielectric constants arising from the thermal agitations of the molecules. The concept of "dipoles" was proposed by Debye mainly because of the experimental observation of this unlooked-for

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[1] For details see: R. Lorenz, "Raümerfüllung," 1921, pub. by Fr. Voss, Leipzig; and also his work on the effect of electric-polar forces upon physical-chemical reactions; K. Fajans, "Die Naturwissenschaften," 1921, p. 729; also original researches of H. G. Grimm, Zeitschr. f. physik. Chem. 1921–1922.

change in dielectric constants with respect to temperature. Using the data available at the time he calculated the dipole-moment for a number of substances. (See table below.) The calculations so made are open, however, to a more or less reasonable criticism, since no consideration was given to the variation of the specific gravity of the substance due to changes in temperature. This phase will be touched upon later in the discussion of the recent work of Isnardi and Graffunder.

A second method, the theory of which was first proposed by Tank and more recently improved by J. Herweg, consists in the investigation of the variations in the dielectric constants with strong electric fields. The latter causes a decrease in the dielectric constants of the molecules in consequence of the orientation of the moment axis of the dipoles.

The third—and, incidentally, the most recent—method for establishing the dipole character of a molecule was devised by P. Lertes, the theory of the method having previously been developed by M. Born. It measures the turning moments produced on liquid dielectric when these are placed in a rotating electric field. These turning moments arise in the liquid dielectrics owing to the internal friction between the free dielectric dipoles and the surrounding liquid as a consequence of which the former cannot respond rapidly enough to the orientating influence of the electric field.

Methods of an entirely different character involve the consideration of the specific vibrations which the "electric centers" execute with respect to one another within the molecule. While investigating the phenomenon of electric dispersions, i.e., measuring the dielectric constant as functions of wave-length, Drude obtained an anomalous dispersion for short electric waves (e.g., in alcohols) accompanied by a marked absorption of these waves. Furthermore, these specific vibrations also depend upon the internal friction of the fluids, i.e., their viscosity. Working, therefore, at very low temperatures where there is a remarkable increase in viscosity, Graffunder was able to transfer the region (short waves) of anomalous dispersion in glycerin to very long electric waves, thus making possible the study of anomalous dispersion under experimental conditions that are more or less easy of attainment.

Investigation of the various phases of these questions distinguished by a fairly reasonable degree of accuracy is possible only because of the marked development in the production of undamped oscillations as is accomplished with the electron tubes of wireless telegraphy. Variations in the dielectric constants as small as 10^{-6} and 10^{-7} of their value may be detected and measured by their means; consequently, no particularly serious difficulties should be encountered in the experimental examination of dielectric constants of gases.

There are evidently many problems of physics and chemistry which, considered in the light of the dipole theory, merit especial interest and experimental investigation. Paramount in importance is the study of molecular structures and of the distribution within the molecule of its electric charges; this is particularly of interest in regard to molecules of organic compounds. Ranking next in importance are the problems of surface tension and adsorption. An acceptable theory of the former has not yet been definitely worked out, although the researches of Harkins on the surface tension of divers bodies may prove helpful. On the other hand, Lorenz and Lande have elaborated a theory of adsorption, based on the dipolar nature of molecules, only the essential feature of which is described here. If adsorption takes place, it does so because a molecule of the adsorbed substance is firmly bound to its electrical "mirror image" in the absorbing surface. With

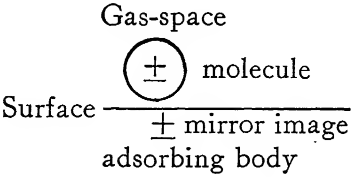

Diagram B

such a conception as a basis a "force law" may be deduced which will entirely accord with the idea of a unimolecular layer of absorbed molecules, an idea first proposed by Langmuir

Dipole Moments of Dielectric Liquids, Vapors, and Gases Determined to the Present Time

Substance	Determined from		
	the Decrease of the Dielectric Constant in Electric Field	the Relation of Dielectric Constants and Temperature	the Dipole Rotation Effect
Ether			
Ethyl ether........liquid	1.20×10^{-18} (Herweg)	14.23×10^{-19} (Isnardi)	12.7×10^{-19} (Lertes)
Alcohols			
Methyl..........liquid	—	Not determinable (Isnardi, Graffunder)	Small moment Magnitude = ? (Lertes)
vapor	—	16.1×10^{-19} (Jona)	—
Ethyl............liquid	—	Not determinable (Isnardi)	5.3×10^{-19} (Lertes)
vapor	—	—	—
Amyl............liquid	—	7.9×10^{-19} (Debye)	8.9×10^{-19} (Lertes)
vapor	—	—	—
Propyl...........liquid	—	5.0×10^{-19} (Debye)	—
vapor	—	—	—
Isobutyl..........liquid	—	6.5×10^{-19} (Debye)	—
vapor	—	—	—
Glycerin..........liquid	—	Not determinable (Graffunder)	2.8×10^{-19} (uncertain) (Lertes)
Carbon disulphide..........	—	No moment (Isnardi)	No moment (Lertes)
Chloroform.........liquid	—	13.6×10^{-19} (Lertes) 12.6×10^{-19} (Isnardi)	—
Carbon tetrachloride. .liquid	—	No moment (Isnardi)	—

TABLE.—*Continued*

Substance	Determined from		
	the Decrease of the Dielectric Constant in Electric Field	the Relation of Dielectric Constants and Temperature	the Dipole Rotation Effect
Benzol Derivatives			
Benzol............liquid	No moment (Herweg)	No moment (Isnardi, Graffunder)	No moment (Lertes)
Toluol............liquid	—	5.1×10^{-19} (Debye) 4.91×10^{-19} (Lertes) Small moment (Isnardi)	6.3×10^{-19} (Lertes)
Nitrobenzol ....liquid	—	5.7×10^{-19} (Debye)	7.1×10^{-19} (Lertes)
Chlorbenzene......liquid	—	—	Moment (value = ?) (Lertes)
Brombenzene......liquid	—	—	Moment (value = ?) (Lertes)
Metaxylol...........liquid	—	No moment (Isnardi)	—
Water..............liquid	—	5.9×10^{-19} (Debye)	7.4×10^{-19} (Lertes)
vapor	—	17.8×10^{-19} (Jona)	—
Gases			
Air....................	—	No moment (Jona)	—
Carbon monoxide........	—	1.18×10^{-20} (Weigt)	—
Carbon dioxide..........	—	3.03×10^{-19} (Jona) 1.42×10^{-19} (Weigt)	—
Sulphur dioxide..........	—	17.6×10^{-19} (Jona)	—
Ammonia.	—	15.3×10^{-19} (Jona)	—

The author acknowledges his thanks to Mr. P. Lertes for the above tabular summary.

in view of certain experimental data. Nevertheless, such a formulation will be beset by serious difficulties; for it is not quite clear, especially as concerns dipole molecules, why other molecules should not become attached, in turn, to the orientated molecule of the unimolecular layer, and thereby effect a condensation of the gaseous substance. Furthermore, positive experimental evidence is not available whereby the validity of a unimolecular layer and its applicability to the adsorption of dipole molecules could be established. At all events, it seems most certain that the water filaments invariably found on glass surfaces are not unimolecular adsorption layers.

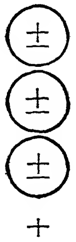

Diagram C

In the above table are presented the liquid and gaseous substances whose dipole character has thus far been investigated together with the scant quantitative data concerning their respective dipole moments, wherever such information is available.

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P. Lertes, Zeitschr. f. Physik. 6, 56, 257 (1921).

The following supplementary remarks may be applied profitably to the data synopsized in this table. After a critical survey and correlation of his own researches and those of other workers, notably of Gans and Isnardi, W. Graffunder concluded that methods involving the measurement of the dielectric constants of liquids as functions of the temperature were not appropriate for the eventual exposition of the dipolar nature of molecules. This is especially so since molecular complexes of unknown composition and configuration are formed in some liquids due to association of their simpler molecules. Dipoles, by their very nature, are favorable to association—after a fashion, a preliminary stage of microcrystalline character. At the present writing it is not definitely known whether or not such a character is in evidence during the solidification of substances like benzol whose molecules exhibit not even the slightest dipole nature. Attention may be directed in this connection to certain experiments of Isnardi in which he has observed variations in the dielectric constant of benzol at temperatures slightly above its crystallization point. This would indicate, under such conditions, the existence of a dipole moment; but since Graffunder's results fail to confirm such a conclusion, further experimental evidence must be awaited.

Judged by its chemical deportment, ether is non-associated in the liquid state. This is surprising indeed because ether appears to have an extraordinarily large dipole moment. Explanation of this anomalous phenomenon will result only from a more scrutinizing investigation of the nature of ether vapor. To all appearances, true dipole moments of molecules may be determined only by the examination of highly rarified vapors. It is very likely, therefore, that the dipole moment for ether—as a rarefied vapor—will not be found appreciably greater than that of other molecules, e.g., the alcohols. As a matter of fact, Jona has already found for methyl alcohol vapor a dipole moment of 16.1×10^{-19}, which is appreciably larger than that of the liquid ether (see table). On the other hand, measurements made upon liquid alcohols yield considerably smaller dipole moments. It seems reasonable, accordingly, to believe that ether, in conformity with its otherwise normal deportment, is characterized by a small dipole moment.

Molecules possessing large dipole moments associate so strongly that much cannot be said about the moment of the individual molecules unless it be examined in the vapor state; furthermore, examination of the substance in the liquid state will yield, because of its molecular association, entirely different results, invariably too small. The method devised by Born and Lertes has been applied, to date, only to liquids and evidently has proven itself meritorious and free from objection.

For the present we must be content with such fragmentary evidences of a corroborative nature as have already been cited. The entire problem is still in its primal development, but nevertheless it doubtless will be productive of interesting and promising results. Appropriate reference may be made at this time to another phase of the problem, concerning which our knowledge, at best, is very limited and obscure, viz.: the study of the friction coefficient of dipoles and ions (R. Lorenz). Although the subject of frequent investigations, very definite and positive information was lacking until very recently as to whether the viscosities of dielectric liquids are influenced by electric fields. Recent experiments[2] have demonstrated that viscosities are not influenced measurably by electric fields; nor is such an influence to be anticipated on a theoretical basis. (Born.) Of more than superficial interest in this respect is the recent work of Graffunder on the shifting of the region of anomalous dispersion in the spectrum of electric waves produced by changes in viscosity; but here again the influence of molecular association upon this phenomenon is decidedly unknown. Furthermore these phenomena are also closely related to the electrical Kerr-effect, the electric double refraction experienced in electric fields. This is particularly true of the dependence of the Kerr-effect upon temperature. Since the phenomenon of double refraction is an effect of the adjustment of the individual molecules, it will depend, obviously, upon the respective molecular fields and upon the disorientating influence of their thermal agitations. Finally the entire question leads to the theory of the Clausius-Mosotti equation of refraction exponents.

As stated before, we have reached only the outposts of a vast experimental field abounding in important problems, whose solutions are of utmost significance for the theoretical development of this phase of modern atomistics.

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[2] Unpublished dissertation by H. Zschiesche, Frankfurt.

CHAPTER V

NUCLEAR DISINTEGRATION

It is generally accepted as scientifically correct that the alpha rays, ejected from radioactive substances, are identical with helium atoms carrying a double positive electric charge. This truth has been established by the classic researches of Rutherford and Royds and of E. Regener. The former investigators demonstrated directly by spectroscopical means that helium made its appearance in glass tubes (Geissler tubes) previously evacuated and into which alpha rays entered by passage through rarefied gas because of their high velocity and consequent high penetrating power. Regener by precision methods of the highest type showed that the charge carried by each alpha-particle is equal to double that of the elemental charge. Since the alpha-particles were found subsequently to be positively charged, it follows (a fortiori), according to considerations to be discussed more fully in Chapter XI, that they are helium ions, i.e., they are identical with doubly ionized helium atoms which have lost their two external electrons. In other words, an alpha particle is an helium nucleus. It would be expected, therefore, that an alpha-particle is characterized by a mass equal to that of an helium atom, which expectation subsequently was fully realized. On the other hand, its dimensions are much smaller than are those of the normal helium atom. Due to their small size and the relatively high velocity with which they are emitted during disintegration, alpha rays possess a great concentration of energy, which can be released on sudden stoppage of the α-particle. Thus, they are capable of penetrating into other atomic systems where they exhibit a high capacity for work when colliding within the interior of the atoms with any of their constituents. If the atomic constituent so affected is an electron which normally is situated in one of the inner electronic shells, an emission of gamma rays, analogous to X-rays, takes place. The existence of these rays may be demonstrated in several ways. Or a partial neutralization of the alpha ray may result, whereby a doubly ionized helium atom is converted into a helium atom with but one charge because of the union of the alpha ray and an electron. On account of its large diameter and high ionization energy (Chap. XI), this singly charged helium atom appropriates to itself very rapidly a second electron from some other atom with which it may collide. In both cases, however, the neutralization results because of an inherent attractive-force (Coulomb). Millikan[1] has carried out some very interesting experiments to investigate the rapidity of such complete recombination.

It may be asked what will happen if the alpha-particles collide with the atomic nucleus itself, rather than with one of its exterior electrons? And further, how shall the term "collision" be interpreted? Since atomic nuclei are positively electrified, a similarly charged alpha-particle, in its approach to an atomic nucleus, will experience a repulsion according to Coulomb's law equal to $-2\epsilon \cdot Z\epsilon/r^2$, where 2ϵ is the charge of the helium nucleus, $Z\epsilon$ the charge upon the atomic nucleus of atomic number Z, and r the distance between the alpha particle and the nucleus. Obviously r varies with the motion of the alpha-particle, having any assignable value from ∞ to a definite minimum value for which the repellent force, as expressed by $-2Z \cdot \epsilon^2/r^2$, has become so large that the alpha particle is strongly repelled from the atomic nucleus, i.e., is deflected from its initial direction. This minimal distance is a measure of the probable size of the atomic nucleus, on the assumption that Coulomb's law is valid for such small dimensions. For many and obvious reasons this assumption is by no means justified, and consequently Coulomb's law fails to contribute to the solution of this important problem of atomic dimensions. It would be more consonant with other facts to describe this minimal distance as a function not only of the nuclear dimensions but also of the law of force operative in the neighborhood of the charges.

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[1] Millikan, Phys. Rev. 18, 456 (1921).

The mutual repulsion experienced by atomic nuclei and alpha particles proved a controlling factor in the eventual proposal by Rutherford of his now classic atom model which, altered by certain ingenious modifications suggested by Bohr, promises to disclose even the minutest detail of atomic structure. The repulsion of alpha-particles is demonstrated experimentally by the dispersion that takes place during the passage of alpha-particles through matter. Upon penetrating a solid body, a parallel alpha beam (i.e., many alpha-particles of the same velocity and the same direction) will be dissipated; in other words, a number of the particles will spread or scatter in all directions due to the repulsion experienced by them when approaching closely to the atomic nucleus of the penetrated substance. This diffusion in all directions is due largely to the unequal extents to which various alpha-particles are repelled, those having approached very closely to the nucleus experiencing the greater repulsion, i.e., the greater angular deflection or scattering. Following their very accurate and pioneer investigations of the varying extents of alpha ray scattering produced during penetration of various substances, Geiger and Marsden concluded that the nuclear charge of a given atom (as proposed by Rutherford) was equal to the atomic number of the respective elements, a provisional finding that has been verified repeatedly by other observers, notably Chadwick. From his studies on X-ray spectroscopy, Moseley deduced a similar relationship.

The question now arises: what happens when an alpha particle approaches very closely to, i.e., encounters the nucleus of another atom? Is all or any part of its energy transferred in any way, e.g., as kinetic energy, to the atom during the collision? As long as it passes through an atom, it imparts no notable amount of its kinetic energy to it, even though the atom so "struck" becomes ionized. William Ramsay was the first to suggest this problem with the expressed idea of utilizing the enormous energy content of a moving alpha ray for the transmutation of elements. To this end he subjected salt solutions to the influence of alpha radiation (radium emanation used as a source) and subsequently examined them spectroscopically. His first positive results failed to be corroborated. The anticipated quantities were not made available in sufficient amounts, nor were the methods employed tested sufficiently and with appropriate care. The more recent data obtained in relation to this question were obtained with an entirely different method; thus, the presence of the individual constituents produced during atomic decay is demonstrated not so much as a material analysis, but rather by their energy effect (e.g., upon photographic plates or by fluorescence).

In an endeavor to find an experimental answer to these queries, Marsden studied the effect produced by alpha particles when projected into an atmosphere of hydrogen. It is well to recall here that alpha-particles give rise to bright specks of light whenever they impinge upon a phosphorescent screen (e.g., of zinc sulphide), each particle producing a single scintillation. The bombardment of such a screen by alpha particles may be viewed through a low-power microscope (spinthariscope). The counting of these scintillations is the basis of the method used by Rutherford for the quantitative determination of the charge on the nuclei of different atoms. The penetrating power, or the range, of the alpha particle is conditioned by the velocity with which it is ejected by the radioactive substance. Obviously, this varies. The average range of the alpha-particle emitted by Radium C is 7 cm.; this means that the scintillations may be observed upon the zinc sulphide screen for distances of 7 cm. or less to the source of the alpha rays. In Marsden's[2] experiments, however, scintillations appeared even when the fluorescent screen was removed to distances beyond the normal extreme range of the alpha-particles, the maximum range thus obtained being approximately four (4) times the normal. The obvious implication is the presence of some substance with a decidedly longer range, a range which the alpha ray normally cannot span. What is the nature of this substance? According to

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[2] Previous reference.

a well-established law, the ranges of projectiles are in direct proportion to the third power of their respective velocities. Evidently the rays responsible for the scintillations at a fourfold range in an atmosphere of hydrogen must be characterized by a velocity 8/5 times as great as that of an alpha particle ejected from radium C. Furthermore, according to the laws of impacting bodies this would indicate a mass of 1 for the ray producing the long-range scintillation, on the basis of a mass = 4 for an alpha-particle (helium). It thus appears that these secondary rays, capable of stimulating scintillations at long range, may be identical in mass with hydrogen. If C denotes the velocity of the alpha-particle at the moment of impingement, C_H that of the hydrogen ray, m the mass of the alpha ray, m_H the mass of the hydrogen atom, then

$$C_H = \frac{2m_\alpha}{m_\alpha + m_H} \cdot C_\alpha.$$

Rutherford subsequently demonstrated directly the correctness of this conjecture by measuring the charge, the mass and the velocity of these rays according to the classic methods used for determining the corresponding factors for positive rays and cathode rays. It has been proved, therefore, that when alpha-particles are projected into an atmosphere of hydrogen, hydrogen nuclei are thrown forward. The details of the mechanism of Marsden's experiment are somewhat as follows. An alpha-particle, while penetrating an atmosphere of hydrogen, will encounter and collide with the nuclear mass of an atom of the hydrogen molecules, bringing about its summary separation from the molecule. Stated otherwise, the hydrogen molecule experiences a dissociation and ionization, as is demonstrated by its eventual high velocity and ionic charge. In view of these observations the rays are termed hydrogen rays, or H-rays. A hydrogen ray is a hydrogen atom ion, i.e., a hydrogen nucleus, since the hydrogen atom consists only of the nucleus and one electron. The direction of these recoiling H-particles is preponderantly that of the alpha rays. Their relative number is small, however, inasmuch as a direct or head-on encounter, which is necessary for H-particle expulsion, occurs but rarely on account of the small dimensions of the nucleus. Glancing (not direct) impacts, as previously stated, produce merely a scattering of the primary alpha rays with or without their simultaneous neutralization.

In view of these astonishing results it was only reasonable to extend this investigation to other elements. Would bombardment with alpha-particles set other atoms in rapid motion (as recoil atoms) in a charged condition, i.e., as ions, as in the case of hydrogen? In an atmosphere of nitrogen and also of oxygen, scintillations were observed at a range of 9 cm., whereas the exciting alpha ray had a characteristic extreme range of only 7 cm. A noteworthy fact was the greater intensity or brilliancy of the scintillations in comparison to those of the H-rays. It seemed very likely, therefore, that the stimulation of the sulphide screen was due to struck nitrogen and oxygen atoms originating in the gaseous atmosphere, i.e., to secondary O-rays and N-rays, analogous to the H-rays. Such a probability is indeed very plausible from the calculations of the ranges of such rays—should these exist—as derived from certain theoretical considerations advanced by Bohr[3] and Darwin.[4] On the assumption that the observed scintillations are produced by rays of oxygen atoms and of nitrogen atoms with single charges, the following calculated ranges are obtained:

For nitrogen	9.3 cm.
For oxygen	7.8 cm.

for primary alpha rays of 7 cm. range.

The existence of high speed rays of the type of the H-rays was not detected; only with helium were a few scintillations of greater or lesser brilliancy detected at longer distances. This observation is in perfect agreement with other results and admirably substantiates the assumption that alpha rays, after impact upon an helium atom, can hurl this forward as a

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[3] N. Bohr, Phil. Mag. 25, 10 (1913).

[4] Darwin, Phil. Mag. 27, 499 (1914).

secondary ray. Accurate measurements subsequently showed that the ranges of the O-rays and N-rays were in fair accord with the calculated values; however, the difference predicted by theory which, on the basis of the aforesaid numbers, should yield for the heavier oxygen atom a 19 per cent smaller velocity, could not be verified. It seems reasonable, therefore, and more expressive of facts, to assume momentarily that the O-rays and N-rays are not actually atomic nuclei of these substances in rapid motion and similar to the hydrogen rays, but rather are they rays of some other mass. Such a conception is justifiable, especially since the more massive oxygen nucleus normally would not be expected to travel as far as the lighter nitrogen nucleus.

These expectations were confirmed by astonishing experimental results obtained by Rutherford; astonishing, because of their theoretical fecundity. Experiments, arranged and performed in such manner as to eliminate from the apparatus even the minutest trace of hydrogen, demonstrated that during bombardment of nitrogen molecules by alpha rays there are produced scintillations due to rays of an extremely great range (exceeding that produced by hydrogen), in addition to the previously observed ray of 9 cm. range. No such long range ray was detected under similar conditions in the case of oxygen. Critical examination of these rays according to the methods applied to H-ray investigation proved conclusively that the secondary rays of long range were identical in mass to the H-ray. In other words, by means of alpha ray bombardment, hydrogen nuclei can be separated from normal nitrogen atoms. The true import of this statement is immense. Briefly, it means the actual disruption or shattering by artificial means of an atomic nucleus yielding an atomic type of an entirely different character. The epoch-making significance of this result is obvious, if we recall that nature has "resisted" hitherto all attempts to decompose elements by artificial devices. We have here a simulation of the natural and spontaneous decay taking place within the nuclei of our so-called radioactive elements. Furthermore, the energy of an alpha-particle is enormously large. Its magnitude may be calculated from the expression, K.E. = $\frac{1}{2}mv^2$, by inserting the corresponding values. Thus, if m, the mass of the alpha ray, is 6.6×10^{-24} grams, its velocity v (range 7 cm.) = 2.0×10^9 cm., sec.^{-1}, its kinetic energy becomes 1.3×10^{-5} erg; or as ordinarily expressed per mole (by multiplying by the Loschmidt number $N = 6.06 \times 10^{23}$, or by using the atomic "weight" 4 in place of the atomic "mass" 6.6×10^{-24}) 8×10^{18} ergs. Stated in the customary calorimetric terms, this is equivalent to saying that during atomic disruption energy is released to the extent of 2×10^{11} g. cal. per mole. The immensity of this energy becomes apparent when compared to the ordinary chemical reaction heats which range from 10^4 to 10^5 cal.

An added evidence that an extreme energy effect of some sort transpires and is operative within the atomic nucleus is had in the surprising observation that the energy of the H nucleus ejected from the atom during disruption, i.e., the H-ray, exceeds appreciably the energy of the primary alpha ray. This, however, was not found to be so in the production of the "natural" H-rays, the ray from hydrogen itself.

A problem of great theoretical import, in so far as it affects most, if not all, of our recent conceptions, may now be proposed. Is a general disintegration of all atomic types taking place as part of the natural functions of our so-called chemical elements? Or are there only certain nuclear types capable of disintegration? Is the nature of their decomposition mechanism the same, or does each element disrupt in a manner peculiar to itself? Finally, what are their respective decomposition products? In this connection thorough search must be made for rays of great range proportionate to the range of the secondary H-rays disrupted from nitrogen nuclei. We will consider here the important researches of Rutherford and of Chadwick.

The experimental procedures adopted for the investigation of long range secondary rays are practically similar in principle and rather simple as regards manipulation. Figure

11 depicts diagrammatically one form of arrangement. The radioactive preparation, *P*, from which alpha rays are ejected, is confined on the head of a movable support which works in and out of a brass shell (somewhat the size of an ordinary match-box). Changes in the position of the support can be adjusted by means of a scale and pointer. The scintillations produced upon the zinc sulphide screen *S* by the rays under examination are observed and counted by means of the low power microscope. The open end of the box, directly in front of the screen *S*, is covered by a thin plate of metal or mica whose stopping power for the rays under investigation is known. It is designated by F_1. For greater filtration of the rays, other plates may be placed between *S* and F_1 at F_2. The substance *M* which is to be subjected to alpha ray bombardment is placed directly in front of the radioactive substance *P*, the alpha ray source. As will be explained in a later section, *M*, if solid, may be used in the form of foil or as a powder. The little chamber enclosing the material and preparation is shielded by a plate of known stopping power, so as to exclude radioactive influences from the interior. The brass box rests between the poles of a strong permanent electromagnet, whose lines of force run perpendicular to the plane of the diagram. By its means the beta rays ejected by *P*, which also stimulate scintillations when impinging upon the zinc sulphide screen, are deflected from their rectilinear path. A continuous stream of oxygen or carbon dioxide, which of themselves do not yield secondary rays under influence of alpha ray bombardment, is drawn through the apparatus.

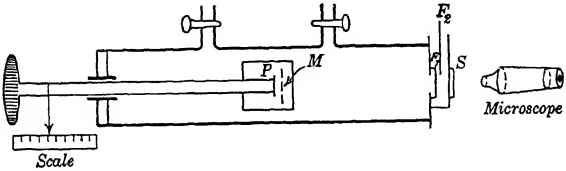

FIG. 11. Atomic Disruption Apparatus of E. Rutherford.

Absorption screens, equivalent in stopping power to definite air distances, may be inserted at F_2, thereby diminishing the length of air space traversed by the alpha particle or by the struck nuclei. The precise determination of the range of long range rays (which in the case of aluminum is as high as 100 cm.) is hereby facilitated. For finer and more accurate measurement of the maximum ranges the smaller air space is progressively increased by a micrometer adjustment, the deviation in position of the alpha ray source being indicated on the scale. Prior to their use, all absorption screens are carefully purified of occluded hydrogen by heating in an evacuated furnace and their stopping power for H-rays determined separately. Then, too, a certain number of long range H-rays are invariably detected in radium C by their scintillations. These may be attributed to minute traces of hydrogen in the radioactive source, or they may arise as a disintegration (?) product from the nucleus of radium C atoms. Whatever their source, their number must be determined and due allowance be made for them when measuring the number of scintillations arising from the presence of other substances, e.g., nitrogen. They are termed "Natural H-rays."

The following diagram[5] (Fig. 12) shows graphically the results of several investigations of ranges. The active substance used in each instance was radium C, whose alpha rays have a range in air of approximately 7 cm. The number of

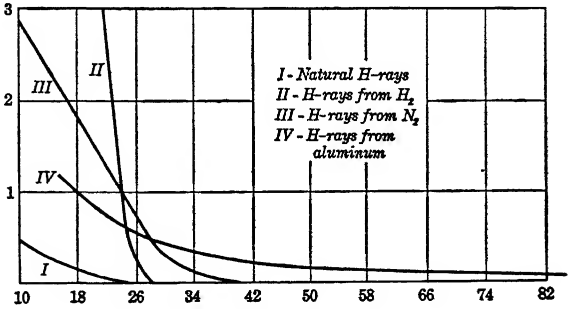

FIG. 12.

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[5] Rutherford and J. Chadwick, Phil. Mag. 42, 809 (1921).

scintillations counted, i.e., the number of H-rays arising per minute per milligram activity of radium C,[6] are plotted as ordinates against their respective ranges as abscissæ. It is necessary that the scintillations be calculated on this basis, since Ra-C has a half-life period of little more than three hours, which means that the number of primary alpha rays decreased progressively during the time of measurement. It will be shown in a later section that the long range rays are actually H-rays, i.e., hydrogen nuclei or positive hydrogen ions (protons).

Curve I shows the scintillations and ranges of the "natural H-rays" when the vessel was filled with dry oxygen gas, which itself, as stated above, is inactive. Curve II is obtained when the oxygen has been displaced by hydrogen gas, the ranges here being due to hydrogen rays expelled from hydrogen molecules. If the hydrogen, in turn, is evacuated and nitrogen introduced (or air, whose oxygen component has been shown to be inactive), scintillations are produced proportional to the nitrogen pressure. Curve III shows the pressure of rays of a still greater range arising from the presence of nitrogen. Finally, Curve IV represents the effect obtained by screening the radium C with aluminum. Here a long range H-ray is observed, almost three times that produced by hydrogen itself. The maximum range, however, is very indefinite since the rays capable of producing it are exceedingly few in number in comparison to those of shorter ranges.

In order to investigate more extensively the origin and the nature of these N-rays (presumably H-rays ejected from nitrogen atoms), the testing chamber was filled with several nitrogen compounds instead of elemental nitrogen. Among the substances tested were such solids as boron nitride, sodium nitride, titanium nitride and parazyan, compounds of nitrogen with elements which themselves yield no secondary rays upon alpha ray bombardment.[7] All these substances

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[6] Measured by γ-ray methods.

[7] Boron nitride. Boron yields H-rays. It is worthy of note that Rutherford, previous to his investigation of boron, found that boron nitride yielded more H-rays

produce rays which are indistinguishable from the H-rays ejected from gaseous nitrogen.

The appended table is a compilation of the results obtained from the first experiments. A mark (cross) placed in front of an element indicates that its disruption was accomplished later.

As is apparent from the table the several elements listed have been investigated both in the simple or uncombined form and in combination. In the latter case, it was obviously necessary to select only such constituent elements as were purified of all traces of hydrogen and whose nuclei of themselves do not yield H-rays when subjected to the action of the swift alpha rays. Usually the oxide, if available, was used as a thin film deposited on gold foil and placed between the screen and the radioactive source. Furthermore, the experiments with aluminum demonstrated conclusively that it is quite immaterial whether the element emitting the H-ray is used in the metallic form or in chemical combination (Al_2O_3). This result is easily comprehensible if we remember: (1) that chemical combination is an action taking place only in the extreme regions of the atoms without any direct influence upon the atomic nucleus, or sensible participation by it in the action; (2) that there are isotopic elements, that is, elements of decidedly different nuclear structure but characterized by the same chemical reactions; and (3) and finally that the heat developed during chemical combination is absolutely negligible when compared to the enormous energy changes taking place during alpha-particle bombardment. Of utmost importance, also, from an experimental point of view, is the success of this method even when the struck substance is brought in powder form directly upon the radioactive preparation ejecting the alpha rays. On the other hand, it is very possible, indeed, that the ranges, obtained when only the pulverized form of the struck sub-

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than was to be expected from its nitrogen content; on that occasion, Rutherford surmised that boron itself contributes to the production of the H-radiation of boron nitride.

HYDROGEN RAYS FROM ELEMENTS

Disengaged by means of α rays from Ra-C (7 cm. range)

Element *	Material of Screen	Number of Particles per min. per mg.	Max. Range in cm. in Air of Atmos. Pres.
Lithium $\left(3, \begin{smallmatrix}6\\7\end{smallmatrix}\right)$	Li_2O	—	—
†Beryllium (4, 10)	BeO	—	—
Boron $\left(5, \begin{smallmatrix}10\\11\end{smallmatrix}\right)$	Elem. as solid	0.15	ca. 45
Carbon (6, 12)	CO_2	—	—
Nitrogen (7, 4)	Air and solid compounds of nit.	0.7	40
Oxygen (8, 16)	Elem. as gas	—	—
Fluorine (9, 19)	CaF_2	0.4	Above 40
Sodium (11, 23)	Na_2O	0.2	ca. 42
†Magnesium $\left(12, \begin{smallmatrix}24\\25\\26\end{smallmatrix}\right)$	MgO	—	—
Aluminum (13, 27)	Metal foil and Al_2O_3	1.1	90
†Silicon $\left(14, \begin{smallmatrix}28\\29\end{smallmatrix}\right)$	Met. powder	—	—
Phosphorus (15, 31)	Elem. as powder; red modification	0.7	ca. 65
†Sulphur (16, 32)	Elem. pow. and SO_2 (gas)	—	—
†Chlorine $\left(17, \begin{smallmatrix}35\\37\end{smallmatrix}\right)$	$MgCl_2$	—	—
†Potassium $\left(19, \begin{smallmatrix}39\\41\end{smallmatrix}\right)$	KCl	—	—
Calcium $\left(20, \begin{smallmatrix}40\\44\end{smallmatrix}\right)$	CaO	—	—
Titanium (22, 48)	Ti_2O_3	—	—
Manganese (25, 55)	MnO_2	—	—
Iron (26, 55.8)	Used as metallic foil	—	—
Copper (29, 63.6)		—	—
Tin (50, 118.7)		—	—
Silver (47, 107.9)		—	—
Gold (79, 179.2)		—	—

* Atomic numbers and atomic weights are given in parenthesis. Numbers placed above one another indicate the atomic weights of the isotopic "pure" elements.

stance was available for examination, may differ appreciably from the true values. Such a difference may reasonably be anticipated because of the peculiar physical condition of the substance. The stopping power of pulverized layers obviously is indefinite and uncertain, because the unavoidable unhomogeneity of such layers renders it well nigh impossible to ascertain their thickness with any degree of accuracy. Nevertheless, this seeming difficulty in no way will prejudice or detract from the main conclusion reached, viz.: that the secondary rays (long range rays) emitted by the various elements, which emit at all, are identical in magnitude for all elements.

The partial data listed in the above table are selected from those investigations which studied secondary rays projected forward in the same direction as the primary alpha rays and having a minimum range greater than 30 cm., the normal range of the natural H-ray as determined not only for gaseous hydrogen but also for hydrogen compounds. With hydrogen as the struck substance practically all of the ejected H-rays were propelled directly forward in the direction of the primary alpha rays. It may be mentioned, however, that for some other substances the existence of long range rays of a retrograde character was also established. The emission of these particles proceeds backward, i.e., in a direction contrary to the primary alpha rays responsible for their disruption from their respective nuclei. (More will be said later about this result.) It is more urgent and important to determine whether or not such substances, from which no long range rays were detected, give rise to shorter ranged rays, i.e., ranges less than the normal H-ray range of 30 cm. Such determinations could be made with sufficient experimental accuracy only in the case of chlorine.[8] For this purpose the apparatus is first charged with carbon dioxide (from which no long range rays are emitted) and the scintillations produced at low ranges observed. These were attributed entirely to the "natural" H-rays obtained from the radioactive preparation

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[8] Phil. Mag. 44, 417 (1922).

and from the absorption filter. The system is then evacuated and gaseous chlorine substituted for the carbon dioxide. Obviously, the presence of any rays proceeding from chlorine with ranges shorter than 30 cm. would be indicated by an increased intensity, i.e., an increased number of scintillations over and above those due to the preparation and absorption plates. No appreciable difference was discernible. It may thus be accepted as definitely proven, at least as far as chlorine is concerned, that there are produced no rays of such short ranges as lie between 16 and 30 cm.

It was remarked above that retrograde H-rays are expelled from certain atomic nuclei under alpha ray bombardment. Such rays were detected for all elements investigated with the remarkable exception of hydrogen itself. The "natural" H-rays produced from molecular hydrogen are projected directly forward in the direction of the primary alpha ray itself. This difference in the directions of H-ray emissions provides added evidence that the H-ray produced in elements other than hydrogen may not be attributed to contamination of these elements by minute traces of hydrogen. Another very remarkable observation showed that the number of retrograde H-rays was nearly equal to those emitted as forward rays, i.e., the intensity was practically independent of the direction in which the alpha ray impinges upon an aluminum foil. Although a considerable number of H-rays are ejected opposite in direction to the alpha rays, their velocity invariably is smaller and the maximum range obtained by them falls short of that attained by the "direct" rays. Obviously, too, this maximum "short" range cannot be determined with a high degree of certainty due to the

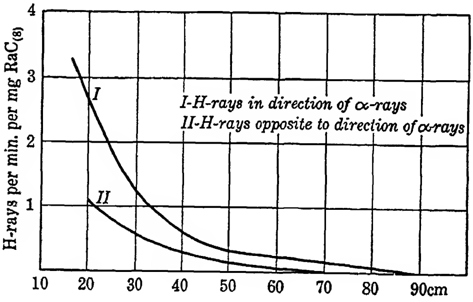

Fig. 13.

relative paucity of the H-rays capable of traveling that range. These data are represented graphically in Figure 13,[9] in which ranges in cm. are plotted as abscissæ against the number of H-rays produced per minute per milligram of radium C. Curve I shows the normal range of "forward" H-rays, obtained from aluminum. Curve II represents the maximum range of "retrograde" H-rays. The relative amount of H-rays endowed with these two opposite motions is obvious.

The following table[10] gives the corresponding maximum ranges observed for H-rays obtained from the substances specified in column 1.

	Maximum Range Forward Ray R_o	Maximum Range Retrograde Ray R_r	$\frac{R_o}{R_r}$
Boron *	58	38	1.5
Nitrogen	40	18	2.2
Fluorine *	65	48	1.35
Sodium *	58	36	1.6
Aluminum	90	67	1.35
Phosphorus *	65	49	1.32

* Designates elements investigated in pulverized form. Values are accordingly less certain.

We may now inquire, and reasonably so, how the maximum range and the number of long range rays emitted depend upon the initial velocity, i.e., the energy of the primary alpha particles producing them. Figure 14 supplemented by the appended table very definitely expresses this relationship of the distribution of the H-rays of various velocities. The sources of the primary alpha rays were thorium C and radium B and C under

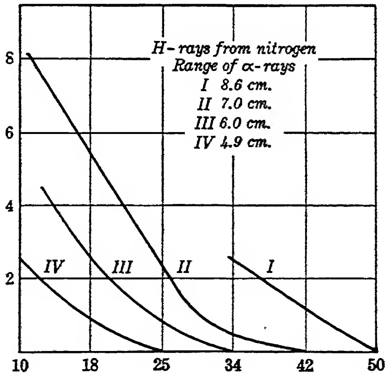

FIG. 14.

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[9] Phil. Mag. 42, 803 (1921).

[10] Phil. Mag. 44, 417 (1922).

various conditions. The corresponding velocities of the alpha rays so produced were 8.6 cm., 7.0 cm., 6.0 cm., and 4.9 cm. The number of scintillations and the corresponding ranges of the H-ray expelled from nitrogen, when bombarded with these alpha rays of different velocities, are represented respectively in curves I, II, III, IV.

Radioactive Source of the Alpha Rays	Maximum Range of Alpha Rays	Number of Alpha Rays with Respect to Radium C	Maximum Range of H-rays from Nitrogen	Number of H-rays at 12 cm.* Distance
Thorium C	66% 8.6 cm. 34% 5.0 cm.	70%	52 cm.	—†
Radium B and C	7.0 cm.	100%	41 cm.	6.5‡
Radium B and C with a gold or silver foil of stopping power equal to				
1.0 cm.	6.0 cm.	100%	34 cm.	3.4
2.1 cm.	4.9 cm.	100%	27 cm.	0.8

* Only H-rays in direction of the alpha rays.

† Measurement not possible because of complications due to the presence of 5 cm. alpha rays.

‡ Corrected for natural H-rays and number of alpha rays.

A marked falling off of the number of H-rays as well as of the range is apparent with decrease in velocity (energy) of the bombarding alpha ray.

Thus far we have selected from the available experimental data, in a more or less random fashion, those essential features which are mutually corroborative and which demonstrate the production of the H-rays from various elements and compounds by bombardment with alpha rays of varying velocity. There now remains the critical question: what incontrovertible experimental evidence may be adduced to prove conclusively that the rays characterized by this long range are in reality attributable to hydrogen? Rutherford alone, and later in conjunction with Chadwick, has carried on researches in this connection in an attempt to ascertain the weight of these particles and thereby prove them to be hydrogen nuclei (protons). Obviously, the direct methods, as applied to the measurement of positive rays and cathode rays, cannot be regarded as feasible for this purpose because of the paucity of the H-ray particles. There is available, fortunately, an indirect method of comparative weighing which is meritorious and applicable to the problem at hand. As cannot be explained here, the deflection of corpuscular rays (charged particles in motion) experienced when subjected to a magnetic field whose lines of force run perpendicular to the motion of the particles, may be expressed by $m \cdot \epsilon / v$, in which m designates the mass, ϵ the electric charge and v the velocity respectively of the particle. It has not been found necessary, to explain satisfactorily the experiments carried out to date, to assume that the long range rays are anything else but hydrogen nuclei; that is, H-rays which owe their origin to the disruption of the nucleus of the bombarded atom. The difficulties encountered in a measurement of these rays are materially augmented by the infrequent occurrence of the H-rays. A high degree of accuracy, under such conditions, is very uncertain, although a remarkable agreement of the calculated and the observed values adds to the reliability of the method and justifies its use. Under any circumstances, however, it must always be borne in mind that the statements enunciated above are founded upon assumptions of a reasonably plausible nature (for example, the calculation of the velocity v in terms of the range) and not upon proven or established facts.

Thus far we have considered the experimental data as obtained by Rutherford alone and in conjunction with Chadwick up to 1922. At this time research was undertaken at the Vienna Radium Institute by H. Pettersson and G. Kirsch to extend Rutherford's work with the prime object of definitely determining the mass of the particles. Attention has been drawn to this topic in a previous paragraph. Moreover, G. A. Stetter[11] (likewise in the Vienna Institute) recently amplified Aston's method of mass spectroscopy (see chapter on isotopes) making it applicable to the examination

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[11] Zeitschr. f. Phys. 34, 158 (1926).

of H-rays, thus rendering it possible to decide by direct experimental measurement the question regarding the velocity of the H-rays. Furthermore, the adoption of a modified method led to the immediate confirmation of the results of the Cavendish Laboratory and to their subsequent extension.

The extension in the experimental data developed in this wise by these Vienna researches may be summarized as follows: all elements are disruptable by means of alpha ray impact and not merely a certain few as was suggested originally by Rutherford.

To date, Rutherford has not subscribed to this viewpoint, even though he later recognized several elements (this is particularly true of the chlorine atoms) as disruptable which were found not to be so in his first experiments. This is especially noteworthy inasmuch as the subsequent disruption of sulphur, a $4n$ atom (that is, its atomic weight is a multiple of the helium atomic weight), compelled the abandonment of his original viewpoint that only elements of uneven nuclear charge (except nitrogen) are disruptable. In view of these discrepancies in the experimental findings of the Vienna Institute and the Cavendish Laboratory it behooves us to scrutinize both sets of data objectively and make a comparative study of their results.

Attention was already drawn to the substantiation of Rutherford's data by Pettersson and Kirsch with a different method. We shall now describe this new method.

The intrinsic difference of this newer method—and obviously an improvement—in comparison with Rutherford's, is the mode of preparation and the eventual form of the substance emitting the alpha rays. Instead of catching radium C upon a metallic plate suspended in the emanation, the latter is condensed in a small tube by means of liquid air. In the preliminary trials the substance under investigation was likewise confined in this thin-walled tube. It was found, however, that the material of the tube (glass or quartz) also emitted H-rays; whereupon the apparatus pictured in Figure 15 was eventually constructed. All parts of this final apparatus were constructed of metal. The wall *F* is of thin copper foil (.01 mm.) upon which were placed in separate chambers the "test substances" I, II, III, in thin powder layers. *E* is the sealed tube containing the emanation. After carefully drying the whole vessel, *E* is shattered by means of the piston *S* working in the movable packing *D*. After the apparatus has been completely charged with emanation, subsequent to the shattering of *E*, the constriction at *A* in the tin capillary is closed and soldered.

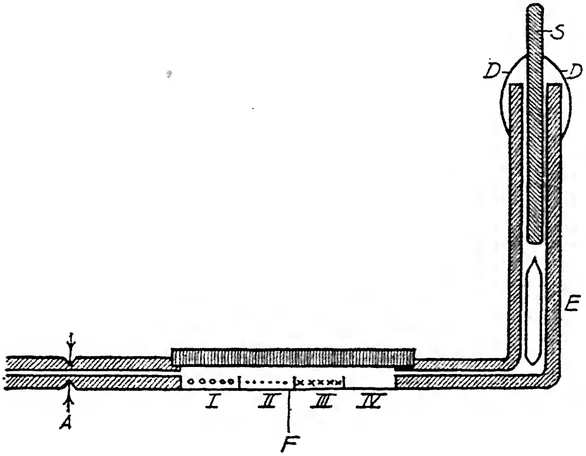

Fig. 15.

The rays emitted by the copper foil are now examined, as in the Rutherford method, by their scintillation effect upon zinc sulphide screens. Each compartment was separately tested, cell IV being the control, for the eventual presence of H-rays, ejected from the copper foil. These were found to be present. Nevertheless, the absorption was such as to compel the assumption that the greater part of these rays, at least from cell IV, were natural H-rays, i.e., hydrogen nuclei arising from residual hydrogen distributed uniformly within the copper. The following Figure 16 depicts graphically the results obtained when the substances beryllium, silicon and magnesium were confined respectively in cells I, II, and III. The data are plotted in a similar manner to the previously shown curves embodying the results of Rutherford's work. The number of H-scintillations counted per minute for each of these substances and for the natural H-rays in the control cell are plotted as ordinates against the ranges in air as abscissæ.

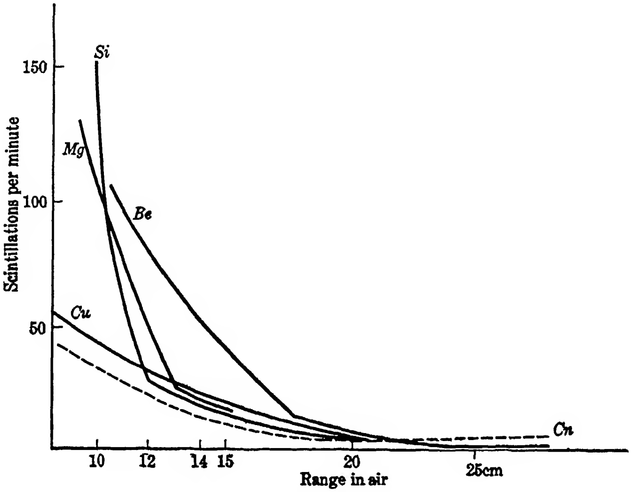

Fig. 16.

In this connection, we may draw immediate attention to a very important point, viz.: the possibility of distinguishing H-scintillations from alpha scintillations. Kara-Michailowa and Pettersson demonstrated that the brilliance of the H-scintillations was substantially smaller than that of the alpha scintillations; they accordingly developed a comparative microphotometric test in which the brilliance of the scintillations under investigation could be compared at pleasure with that of the alpha rays.

In this manner beryllium, silicon and magnesium were proven to be disruptable, the corresponding maximum ranges of the H-rays emitted from them having the approximate values as shown below.

	Beryllium	Silicon	Magnesium
Rmax. ~	20 cm.	15 cm.	16 cm.

Rutherford and Chadwick subsequently verified the results of Pettersson and Kirsch as regards the disruptability of magnesium and beryllium.

Let us fix our attention, for a moment, upon the dotted curve drawn below the "copper curve" of cell IV in Figure 16. This is the theoretically calculated curve for copper on the assumption that the H-rays from copper arise only from the hydrogen present in the copper, i.e., they are solely natural H-rays. Somewhat later Pettersson and Kirsch were of the opinion that they had isolated H-rays from copper itself, a contention disputed by Rutherford. The same applied to nickel.

Rutherford and Chadwick, thereupon, began a new series of experiments in which they detected (in addition to the elements already specified on p. 80) H-rays of ranges varying from 16 to 30 cm. arising from the following elements. Their relative abundance, on the other hand, was much smaller (1/3 to 1/20 that of the H-ray from aluminum).

Neon—Magnesium, Silicon—Sulphur—Chlorine—
Argon—Potassium

Absence of H-radiation was established with certainty for the following elements: helium, lithium, carbon, oxygen. The results obtained for elements from calcium to iron proved doubtful and unreliable. Negative results were obtained in the cases of nickel, copper (both of which were found positive by Pettersson and Kirsch), zinc and selenium (positively by Pettersson and Kirsch), krypton, molybdenum, palladium, silver, tin, xenon, gold, uranium.

On the other hand, the observations of Kirsch and Pettersson indicate with certainty that the following elements are positively H-radiating: beryllium, carbon, oxygen, titanium, vanadium, chromium, iron, selenium, zirconium. These elements, however, emit only very short-ranged H-rays. Methods hitherto in use are not adaptable to their ready investigation and their subsequent measurement, if they lie within the range of the primary alpha rays, for the presence of the fewer H-rays is masked completely by the extraordinarily larger number of alpha rays.

A method was elaborated, however, for their detection, based—as it seems—upon a theoretically obvious and extremely important consideration. The scattering of alpha rays, i.e., the deflection from their initial directions experienced when approaching closely to other atoms, is due to the mutual repulsion established between the positive atomic nuclei and the positively charged alpha rays (Coulomb's Repulsion). The closer their ultimate proximity to one another, the greater the angle of deviation of the alpha ray, which for a "head on" or "direct" collision may be 180 degrees. A deflection of 180 degrees means a reflexion of the alpha-particle in a direction opposed to its initial direction. Kirsch and Pettersson now observed that these particles are absent for just those atoms which suffer disruption by a "direct" or "head on" impact; retrograde alpha rays of very short range only are observed. On the other hand (as stated above according to Rutherford's data), H-rays arising from the disrupted atoms are emitted fairly uniformly in all directions. This obviously suggests a possible method to measure the retrograde H-rays (the H-rays emitted in a direction opposite to that of the alpha rays), even when these are very close to the substance under investigation, without an undue masking interference because of the abundance of the primary alpha rays. Figures 17 and 18 indicate how this newer method differs from the older.

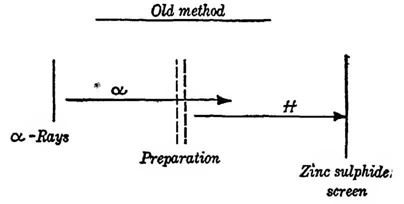

FIG. 17

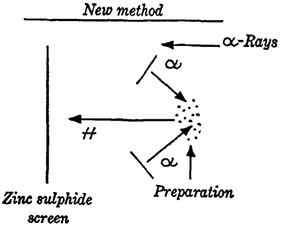

FIG. 18.

Using this method (a similar one having been devised since by Rutherford and Chadwick), Kirsch and Pettersson have found a large number of the elements capable of emitting H-radiation, which led them to the conclusion that all elements are disruptable by alpha ray impact. Among the first twenty elements none was found which did not yield H-rays.

Rutherford questioned these measurements on the basis of experiments carried out by Bates and Rogers which tended to show that Ra-C emits other rays of greater ranges, viz.: 9.3 cm., 11.2 cm. and 13.3 cm., in addition to the normal alpha ray of 7.0 cm. range. In toto, this objection could not be maintained; for Rutherford and Chadwick themselves demonstrated subsequently the non-existence of the 13.3 cm. range alpha ray; furthermore, it was observed also that the 11.2 cm. ray occurred much less frequently than was at first assumed. Kirsch and Pettersson, in turn, were unable to confirm Rutherford's conclusion as to the existence of the 9.3 cm. ray, they finding them much more abundant in oxygen than in an atmosphere of nitrogen. Explanation of this difference is still lacking. To all appearances, the correctness and the reliability of the experiments of the Vienna Institute are assured by the photometric test of the brilliancy of the respective scintillations. Rutherford is of the opinion that Kirsch and Pettersson failed to detect the 9.3 cm. rays because of poor absorption filters for the 7.0 cm. ray, while the latter observers assert that Rutherford's 9.3 cm. rays were mistaken by him because of "thin" spots in his absorption plates. There is thus much occasion for doubt. Further to accentuate the reasonableness of this doubt, we cite here the recent findings of L. Meitner and K. Freitag. Using Wilson's condensation method, these observers discovered long range alpha rays ejected from thorium C with ranges of 11.3 and 9.3 cm., the former appearing much more abundant than the latter. It is exactly these ranges which Rutherford finds for the long range alpha rays from Ra-C.

This uncertainty, however, is confined essentially to the question as to the number of possible disruptable atoms and to the existence of H-rays of small range, which are wanting according to Rutherford but which are rather numerous according to Kirsch and Petterssen. As evidence of the actual disruption of atomic nuclei, we must consider and accept all positively established results. The question immediately arises: what may be concluded from these data concerning the structure of the atom and of the nature of the forces operative within it? The following facts have thus far been established: the emission, in all directions, of H-rays ejected not from hydrogen molecules alone, but from higher atomic nuclei also; the relation between the ranges of H-rays and the velocity of the primary alpha rays responsible for their ejection; the greater range of the H-ray expelled from the higher atomic nuclei as compared with that peculiar to the "natural" H-rays; the paucity of the H-rays derived from the atomic nuclei compared to the greater number of "natural" H-rays (e.g., 20 times greater than obtained in case of nitrogen).

Let us discuss Rutherford's conclusions.

The nucleus of the disruptable atom, accordingly, may be visualized as comprised of a H-nucleus bound in such very loose combination with the rest of the nucleus (one or more helium nuclei) and situated exterior to it, so that an alpha-particle which has penetrated into the atom may concentrate its entire energy upon the H-nucleus. Atomic nuclei of such elements thus would be characterized as having satellites of H-nuclei, i.e., constituents not firmly attached to the nucleus and hence readily removable. The nuclear constituents of a non-disruptable atom, on the other hand, are so strongly and closely bound mutually that the energy imparted as a result of an alpha ray encounter is distributed over the entire nucleus. As a consequence, no one individual constituent absorbs sufficient energy to liberate it from this union. Moreover, during the process of disruption, due to the alpha ray bombardment, the total kinetic energy of all atoms taking part in the disruption is greater after than before the bombardment. The accompanying emission of H-nuclei, evidently, takes place not only at the expense of the energy imparted by the alpha ray, but it can absorb, in addition, a rather considerable amount of intra-atomic energy from the disrupted nucleus itself. Calculations indicate that the most rapid H-nucleus from aluminum obtains energy to the extent of 40 per cent from the energy of combination of the nucleus. Only in the case of nitrogen does a loss of energy (13 per cent) take place. Obviously, nitrogen owes its exceptional behavior to a firmer and more compact union of the disruptable H-nucleus to the residual components of the nucleus. The paucity of the very rapid H-rays must be stressed especially in comparison to the total number of H-rays emitted from aluminum. By far the greatest portion of them are emitted therefore from aluminum with attending loss of energy. A few more pertinent remarks will be added later in the discussion of Rutherford's Satellite hypothesis as compared to the Explosion hypothesis advanced by Kirsch and Pettersson. We must not, however, overlook one definite point in this problem of the long range H-ray. As we know, the ranges of H-rays are readily measurable experimentally. From this measured value, the velocity, v, of the ray is calculated by means of the Geiger-Nuttall formula $R = av^3$. This relationship of range to velocity has been found valid for alpha ray measurements. In the above results on a-rays, the assumption was tacitly made that it applied likewise to H-rays, whereby the calculation of their velocities is readily made from their respective ranges. It is not surprising that we have succeeded, thus far, to formulate only the most general notions in so difficult a subject as nuclear disruption. Rather, we should be amazed at the unexpected results, so thoroughly radical and novel in contrast to the older view of the nature of matter, revealed to us by the highly gifted and resourceful intuition and faultless experimental technic of Rutherford.

Nuclei of hydrogen and of helium may be considered, with reason, to be the primal mass constituents, the "bricks," of atomic systems. This means that the atomic nuclei are aggregates in various proportions of H^+ (proton) of mass = 1 and a single positive charge, He^{++} (alpha ray) of mass = 4 and carrying a twofold positive charge.

Obviously, if we adopt the H-nucleus as the universal and ultimate constituent (or brick), the helium nucleus (or the alpha particle) will be comprised of four protons and two electrons. Thus far experimentation has failed to detect a nucleus consisting of two hydrogen nuclei and one electron; nor has the slightest evidence been adduced, to date, to establish the existence of one hydrogen nucleus coupled with but one electron, i.e., a hydrogen atom of exactly nuclear dimensions. The latter may be interpreted as an element corresponding to atomic number = zero. We ask, therefore, how it is at all possible to demonstrate conclusively the existence of such an element. Our present inadequate knowledge apparently indicates the experimental impossibility of establishing the existence of so small an atom and possessing such extreme penetrating power and characterized by total absence of exterior electric behavior. Apropos of this, Rutherford recently has pointed out that the peculiar trend of modern atomic physics demands the assumption of such neutral nuclei, mainly because it is difficult to perceive how a larger atomic nucleus may be constructed out of smaller similarly electrified nuclei in opposition to their enormous mutual electrostatic repulsion.

Pettersson characterizes Rutherford's views as a "Satellite hypothesis" largely because these views hold it essential that the H-rays do not originate from a firmly bound atomic nucleus, but rather from a loosely annexed unit somewhat in the manner of a satellite. The main support of this hypothesis may lie in the fact that the number of H-rays (or what may be taken as equivalent, the number of effective alpha ray impacts) is very small, much smaller than that of the natural H-rays. This is questioned by Pettersson[12] who offers an alternative explanation for the mechanism of atomic dis-

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[12] H. Pettersson, Proc. Phys. Soc. London, **36**, 194 (1924).

ruption. His views are termed "Explosion hypothesis." He cannot disregard, however, the paucity in numbers of the H-rays. His explanation is somewhat as follows: only the very rapid H-rays are so infrequent but that the total number of rays increases manifoldly if the slower H-rays (those of shorter range) are considered also. The existence of these is definitely established by the results of his experiments in the Vienna Institute. In addition, the "Satellite hypothesis" seems untenable to him inasmuch as he considers all atomic nuclei disruptable, especially those whose atomic weight is a multiple of helium, e.g., C(A = 3He), O(A = 4He), S(A = 8He). The disruptability of these last named elements was verified likewise by Rutherford. The "satellite" structure of such a "multiple helium" nucleus presents at best a very cumbersome notion of nuclear structure. It must be recalled here that the atomic weight of sulphur departs appreciably from the 8-fold value of Helium: 32.07. There remains still one more point of interest as regards Rutherford's views: the conclusion drawn from his latest disruption experiments (which likewise is in agreement with the "Explosion hypothesis") that the ranges of H-rays from elements with even atomic number are smaller (i.e., the energy released during disruption is smaller) than the range of the rays from elements of uneven atomic number.

As a final consideration we may ask if it is at all possible to combine the "satellite" hypothesis and the "explosion" hypothesis, and whether they are really mutually contradictory. It has been assumed tacitly, thus far, that each effective nuclear impact causes the ejection of but one H-ray. It follows, as a consequence, that the emission of the H-nucleus may be viewed as the effect of a direct impact. The assumption advanced by Pettersson is of decided greater appeal, viz.: the nucleus as a unit takes up the impact energy of the alpha ray, whereby it is transposed into an intermediate unstable condition of greater energy content, as a consequence of which it "explodes" or disrupts. If the entire energy be imparted to one H-nucleus of the atomic nucleus (a loosely bound nucleus according to Rutherford), obviously this will be ejected with the total energy content or, as stated above, with even greater energy. Or, a "firmly bound" H-nucleus may also be ejected with smaller energy content; and finally it is even possible that several particles may be ejected simultaneously from the same atomic nucleus. This would explain the presence of the rather large number of H-rays of smaller range, whose existence was first shown by Pettersson's method. It is reasonable indeed to anticipate an experimental solution to this problem. Blackett has already shown that a very important question may be investigated in this connection: the eventual fate of the impacting alpha ray. He has shown (by Wilson's condensation method) that the alpha ray after impact upon the atomic nucleus does not continue in its path, but to all appearances it remains "bound" to the impacted nucleus, or with the residue thereof. It is altogether very possible, therefore, that the result of an impact may be the cleavage of a H-nucleus from the impacted atomic nucleus and the subsequent addition to it of a helium nucleus. In other words, there would result a "building up" process, a synthesis, into higher atomic forms, and not a disruption into "lower" constituents. We can hopefully anticipate, therefore, that it will be demonstrable whether the slow H-rays are emitted separately or collectively from an impacted atom.

Perhaps the successful isolation, not only of the ejected H-ray, but the isolation also of its counterpart, the atomic residue, may eventually be accomplished. As is apparent, such an experimental accomplishment is of paramount significance; for only in the light of its results may a positive statement be made concerning the true and ultimate constituents of atomic nuclei and their mutual inter-relations. Since the new methods of Pettersson and Kirsch, as well as that of Rutherford, are not yet completely exploited, we conclude the brief discussion of this most fascinating and important phase of atomism with the hope that further experimentation of a more decisive nature soon will be forthcoming; for by their means alone will it become possible to bridge the gaps of certain experimental shortcomings and satisfactorily explain apparent inconsistencies between theory and experimental data. Until this definite information is available, it is highly recommended that premature and hasty constructions of atom models be avoided.

CHAPTER VI

The Fundamental Unit of Electricity

By the concept of "elemental quantity of electricity" we understand the smallest indivisible electric charge, the fundamental magnitude of which all other charges are multiples. The existence of such an elemental unit was conjectured by H. v. Helmholtz[1]—first advocated by him in his "Faraday Lectures" at the Royal Institution[2]—on the basis of the laws of electrolysis.[2a] These laws (first enunciated by Faraday in 1826) state that each and every ion transports, during electrolysis, a definite minimum of electricity, or an integral multiple of it, proportionate only to its valence and independent of its chemical nature, whether this be atomic or molecular. (Equi-valent ions, therefore, are those that convey equal quantities of electricity.) Experiment has demonstrated repeatedly that the quantity of electricity transported during electrolysis by a gram molecule of any univalent ion is 96,560 coulombs. This magnitude is called a faraday. If a gram mole contains N ions (Loschmidt number) each of which is associated with an equal charge ϵ, the following simple relation will obtain (whereby the fundamental ionic charge is readily calculable):

$$N_\epsilon = 96{,}560; \quad \text{and} \quad \epsilon = 96{,}560/N.$$

As a consequence of the very precise experimentation of Thomson, Wien, Rutherford, Millikan et al., with cathode rays and β-rays from radioactive substances, we are now in a position to determine very accurately the ratio ϵ/μ as a

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[1] Ann. Physik. 11, 737 (1880).

[2] "Now the most startling result of Faraday's Law is perhaps this: if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

[2a] G. Johnstone Stoney expressed similar views some ten years previously.

characteristic magnitude of the corpuscular rays comprised of electrons. Here ϵ is the electric charge of the individual particle of the ray (electron) and μ its mass. This ratio, so determined, proves to be 1.769×10^7 electromagnetic units, or 5.307×10^{17} electrostatic units; subsequently, the quantitative determination of the so-called Zeeman Effect, the resolution of spectral line when in a magnetic field resulting from the influence of the magnetic field upon the electronic motion, demonstrated the correctness of these values.

Somewhat later the same values were obtained for this specific charge of the electron, as the ratio ϵ/μ is commonly termed, for electrons emitted by metals when illuminated by rays of the proper frequencies (photo-electric effects) or when elevated to higher temperatures (thermions) (Chap. VII).

Positive rays, which make their appearance in discharge tubes under proper experimental conditions, also were recognized as electrified gaseous ions and their corresponding ϵ/μ values subsequently ascertained. The mass peculiar to the individual particles constituting these rays may be determined without serious difficulty since their chemical nature is revealed definitely by their spectra. Knowing, therefore, the mass m of a positive ray particle and the ratio of its charge to mass e/m, the determination of the magnitude of the charge e inherent in each particle becomes a matter of simple computation. For hydrogen positive rays—rays produced when the discharge tube contained hydrogen gas—this calculated value was found identical to the value e, obtained for hydrogen during electrolysis on the basis of Faraday's law and Loschmidt's Number. In all electrolytic phenomena there is a constant recurrence of this charge or some simple multiple of it, depending upon the valence of the electrolytic ion. In somewhat the same manner all positive rays, irrespective of their nature, exhibit the characteristic charge e of the hydrogen positive ray, or some small multiple of it.

Then too, it was shown by E. Meyer and W. Gerlach,[3]

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[3] E. Meyer and W. Gerlach, Arch. d. Gen. 35, 398 (1913); Ann. d. Phys. 45, 177 (1914).

and somewhat later by A. Joffe,[4] that the variations in the charges of ultramicroscopic metallic spherules occasioned by the influence of radiations of the proper wave-lengths are likewise expressible as whole multiples of some unit charge of the same order of magnitude as the elementary quantity of electricity derived in electrolysis. During the two decades just passed, theoretical considerations have stressed the necessity and the significance of assuming the existence of such an elemental unit charge. During the same interval experimental technic has kept abreast with these developments and the consequent demands made upon it by the newer theory. Experiment has fully confirmed the correctness of the speculative considerations which gave rise to the concept "electron," and as far as experimental accuracy will permit, the various procedures, elaborated for the measurement of the electronic charge, all yield the same numerical value for this fundamental unit.

Methods have been devised by several investigators to ascertain exactly the numerical value of this unit charge. To J. J. Thompson, however, great credit should be accorded for the elaboration of a method the essential features of which eventually suggested the ingenious device of F. Ehrenhaft and R. Millikan. This latter method, in principle, consists of the following: a very small spherule of metal or of wax or of some similar substance (in Millikan's later experiments he employed droplets of oil) is introduced between two parallel plates, placed horizontally and isolated from one another electrically. The particle is then illuminated laterally by a powerful stream of light and its movements observed by ultra-microscopic methods. Obviously, the gravitational attraction will exert upon the spherule a force of mg dynes, where m is the mass of the spherule ($m = \frac{4}{3}\pi a^3\sigma$, where a is the radius and σ the specific gravity of the particle). In other words, the particle will fall toward the lower plate and its time of descent may be noted. If the particle is electrified with a charge e, its

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[4] A. Joffe, SB. München. Akad. 1913, p. 19. Later, also, R. Bar, Ann. d. Phys. 57, 161 (1918).

rate of fall will not be influenced to any appreciable extent, provided the two horizontal plates themselves are uncharged. However, if an electric field be impressed, the observed rate of fall fluctuates, depending at any one time upon several factors. Assume a difference of potential of V volts to be impressed upon the plates, which now serve as a condenser. The electric field E so produced for a distance d between the plates would be in static C.G.S. units (1 C.G.S. unit = 300 volts),

$$E = V/300d,$$

and the force acting on the charge e (of the particle) is then Ee. According to the charge of the particle (its magnitude and sign) this force Ee may accelerate or decrease the initial rate of fall of the minute particle. For example, if the potential difference were so impressed as to give the upper plate a charge of the same sign as that upon the spherule, the latter would fall more rapidly; on the other hand, assuming the plate to be oppositely electrified, the particle practically remains at rest if the applied potential difference just neutralizes the gravitational influence. If the former proves to be greater, the particle will rise. Assume, for the moment, that the field E is so chosen that the electric force acting on the charge is opposed to, and equal to, the gravitational force exerted upon the mass. Under such conditions,

$$Ee = mg \qquad (E = \text{Halt potential})$$

and the particle "floats" between the condenser plates. Knowing E, m and g, e may be calculated. Further, if we assume the existence of an elemental unit charge ϵ, the observed charge e of the particle is

$$e = n\epsilon.$$

To calculate ϵ, therefore, the mass of the spherule (or droplet) must be known. Because of its exceedingly small weight, this mass is not determinable directly by any of the ordinary methods of weighing.

Nevertheless, the method, as described above, permits a satisfactory solution of the problem inquiring into the very existence of this elemental charge and its magnitude, i.e., the atomic structure of electricity. It accomplishes this without first determining the mass m. Suppose[5] the charge e_1 ($= n_1\epsilon$), inherent in the particle, to be changed to e_2 ($= n_2\epsilon$); evidently, this would necessitate a readjustment of the electric field from E_1 to E_2 so as to compensate for this variation and ultimately to attain equilibrium with the gravitational field. If the mass remains constant, these various changes bear to one another the relation (from $e = mg/E$)

$$e_1 : e_2 : e_3 = 1/E_1 : 1/E_2 : 1/E_3 \cdots.$$

Granting the existence of the fundamental unit of electricity (ϵ), this may be written as:

$$n_1 : n_2 : n_3 = 1/E_1 : 1/E_2 : 1/E_3.$$

This last continued proportion is markedly significant. Interpreted correctly it states: if electricity is granular in structure and if there is an elemental unit, as certain theoretical exigencies demand, then the reciprocal values of the several compensation fields E_1, E_2, E_3, etc., must bear to one another the relation of simple whole numbers.

This interpretation is the only logical inference that may be drawn from all the available experimental data dealing with this important phase of atomistics. F. Ehrenhaft, alone among a number of investigators, on the strength of certain experiments of J. Parankiewicz,[6] has doubted the existence of an elemental charge. The failure of Parankiewicz to find small whole numbers as expressive of the relation of the charges upon similar particles may be ascribed largely to the Brownian movements of the small particles, which are too

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[5] Changes in charge may be brought about, for example, by ionizing the air in the condenser by means of radium and then waiting until the particle "catches" a gas-ion (Millikan) or by illuminating the particle with ultra-violet light, whereby it becomes charged positively by the photoelectric effect.

[6] For a minimum value Parankiewicz found for the charge a value of 2.68×10^{-13} or about 1/1800th part of Milliken's quantum. See below. Tr.

great in proportion to the distances employed while observing the motion of the particle. As a consequence, the observed time of falling becomes more erroneous. The "Haltpotentials" E_1, E_2, etc., were not found directly by Parankiewicz, but by interpolation between two values, for one of which the particle still falls (predominant influence of the gravitational field), while for the other it rises (predominant influence of the electric field). The square of the mean displacement $\bar{\lambda}$ of a particle in a definite direction per second may be obtained from Einstein's equation for Brownian movements, $(\bar{\lambda})^2 = 2RT/N \cdot B$, where R is the gas constant, T the absolute temperature, N the number of molecules in the mole, and B the mobility of the particle. In order that the Brownian movements may not disturb the motion of the particle, the displacement of the particle due to it must be small in comparison to its displacement during the same time interval under the differential influence between the gravitational and electric fields. This condition does not obtain in Parankiewicz's experiments and consequently the objection raised against the atomic structure of the electric charge is unfounded.

To determine the absolute magnitude of the charge, it is necessary that we first know the mass m of the particle, i.e., its radius and specific gravity. To calculate these quantities, recourse is had to several theoretical laws: the law of Stokes, the Brownian movements of small particles, and, finally, the law expressing the relation of color of diffracted light to size of the diffracting particles. With their aid, the radius a of the particle may readily be evaluated. Combined with the specific gravity σ of the material this leads to the eventual determination of m.

Stokes' hydrodynamic law is of special importance. Thus, a small particle, falling under gravitational attraction, in a medium opposing the motion of the particle with a definite friction, will not be accelerated; rather, its mobility will be characterized by a constant velocity V which is determinable from the coefficient of friction μ of the medium, the radius

a of the falling body, and the gravitational force K acting upon it according to the equations:

$$K = 6\pi a\mu v; \quad K = mg = \tfrac{4}{3}\pi a^3\sigma g.$$

Strictly speaking, this law is valid only for a continuously resistive medium of infinite expansion. To apply it to gas, which obviously is not a continuum, but is composed of molecules whose spacing is of the order of magnitude of the particles in question, it becomes necessary because of certain considerations arising from the kinetic theory of gases, as proposed by Cunningham, to multiply the force K by a corrective factor $(1 + A(\lambda/a))$. In this correction factor, λ is the free path of the particle of radius (a) in a medium in which it is falling and A is an empirical constant whose value lies between 1.63 and 0.815. Its value depends in some way upon the nature of the collisions between the particles and the molecules of the surrounding medium. It has been shown experimentally that this formula, as stated, is limited in the range of its applicability, being valid for such cases only in which the ratio λ/a is less than 0.4 ($\lambda/a < 0.4$). More will be said about this later.[7] Under any circumstance, however, it is well to remember that Stokes' equation is derived from hydrodynamic principles, whereas Cunningham's corrective factor is based upon gas kinetic considerations.

Following upon Millikan's researches, as a result of which the existence of the elemental unit of electricity was definitely proved and the magnitude of its charge accurately measured, F. Ehrenhaft has endeavored, by means of numerous and extended experiments beginning in 1910, to demonstrate not only the incorrectness of the value for ϵ as determined by Millikan, but to cast doubt upon the very existence of such a unit charge. In any event, the experiments of Millikan, as interpreted by Ehrenhaft, are not sufficiently conclusive to be acceptable as an ultimate and incontrovertible proof of the existence of the electron.

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[7] See also E. Meyer and W. Gerlach, Elster Geitel Festschrift (verlag Vieweg, 1914), and W. Gerlach, Physik. Zeitschrift, **20**, 298 (1919).

We know today from various sources that the objections raised by Ehrenhaft are not valid. The outcome of numerous experiments of a highly critical character has fairly definitely established that ionic charges are whole multiples of some fundamental unit. (Stated otherwise, there is an indivisible and ultimate atom of electricity corresponding to the charge 4.77×10^{-10} E.S.U.) In Ehrenhaft's experiments, however, the particles became charged because of the assumption by them of just such gas ions present within the condenser space. The results obtained by him under such circumstances, viz.: that the various particles were promiscuously charged, i.e., the charges associated with them do not bear to one another a relationship expressible in simple whole numbers, thus become unintelligible and suggest the intervention of some reaction whereby the anticipated effect is entirely obscured and vitiated. Furthermore, it was subsequently shown that his data had been acquired on the basis of incorrect assumptions. After investigations extending over a period of many years by a number of workers, two points were recognized as subject to contradiction: these are, the nature of the particles and the validity of the application of the Stokes-Cunningham law. Attention had been focused upon these two points as early as 1910 by W. Kaufmann and M. Planck.[8] A positive experimental proof of the sources of error as yet undetected was first proposed by E. Meyer and W. Gerlach [9] following their direct determination of the radius of an isolated metallic particle of ultra-microscopic dimensions and unknown density when this was permitted to fall under various pressures within the condenser space.[10] The laws expressing the rate of fall of small spheres obviously show a constant relation between the radius of the falling sphere and its free path, that is, the pressure of the surrounding gas. The velocities of falling spherules depend upon both these factors, increasing with increased radius and with diminishing pressure. To observe

[8] Phys. Zeitschr. 11, 940 (1910). Discussion on Ehrenhaft's lecture, "Naturforscherversammlung Königsberg."

[9] Elster-Geitel-Festschrift, 1915, 196.

[10] E. Meyer and W. Gerlach, Ann. d. Phys. 47, 227 (1915).

the effect produced by pressure alone it is but necessary to keep constant the other variable (radius) during the observation. This is accomplished by noting the relative velocities of the one and the same particle when surrounded by atmospheres of various pressures. A series of such measurements may serve indubitably to test the validity of the theoretical laws of falling spherules. To confirm any one law, the value of the radius *a*, as calculated from the data of these observations after substitution in the proper formula, should be independent of the gaseous pressure at which its velocity was observed.

Not one of the numerous laws thus far proposed entirely fulfilled this condition. It may be stated, however, that this shortcoming in no way indicates the non-validity of the individual laws. It is not possible sharply to distinguish between the absolute non-validity of a law and its apparent non-validity as evidenced by the failure of its formula to yield constant *a* values. The latter possibility (viz.: the inconstant values for *a*) may arise very easily if false values have been inserted for the specific gravities of the particles in the formulæ from which the radius is to be evaluated. It is altogether likely, indeed, that the specific gravity of the compact material as ordinarily known ought not be accepted to evaluate the mass (i.e., the radius) of small particles. Thus, measurements made for platinum particles dispersed in an electric arc at pressures between 760 mm. and 30 mm. of Hg yielded, according to one of the laws, constant values of $\sigma = 11.56$ in place of the normal value 21.4.

The inquiry into the density and the constitution of ultramicroscopic particles that has arisen because of the discrepancies outlined in the previous paragraph has been developed from many points of view. Schidlof and his students, notably A. Targonski, have shown that the specific gravities of small particles were altered considerably after frequent remelting.[11] It was also noted that particles pro-

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[11] To accomplish this a method proposed by Einstein and first tested by Weiss is employed: the particle is allowed to fall slowly through a sensitive electric furnace heated to high temperature; even silver particles melted.

duced by volatilization in the electric arc or by electrode dispersion in the spark do not present the appearance of a rigidly cohering and compact mass but rather they appear sponge-like in structure. Still another factor must be considered as regards small metallic particles, especially metals of high melting points. It is certain that even the more compact particles, produced by the methods mentioned above, exhibit irregularities in their surfaces. When these superficial inhomogeneities are of very small dimensions compared to the diameter of the particle, then only do the assumptions of Stokes' law become valid and the law itself applicable.

An entirely different conclusion was drawn by E. Regener from experiments of Ernst Radel,[12] designed to determine the existence or the non-existence of a "subelectron," i.e., an electric charge of smaller magnitude than the electron of Millikan. Using Radel's data, Regener proposes several reasons why Ehrenhaft's experiments mislead to the concept "Subelectron." The materials used in these investigations were particles of paraffin oil, rosin, gold and mercury. Direct measurements of the charges carried by particles of these respective substances demonstrated that all particles with diameters larger than a definite minimal value were associated with the same quantum or unit charge, whose magnitude was in perfect agreement with Millikan's elemental unit. On the other hand, below this critical value the decrease in the radius causes a proportionate decrease in the magnitude of the charge, as may be judged from the curves given in Figure 19 which represents the data obtained for gold. Here the magnitude of the charge is plotted as ordinate against radii of the gold particles, calculated according to the Stokes-Cunningham law, as abscissæ ($A = 0.815$). It is apparent that Millikan's quantum, or an integral multiple of it, was

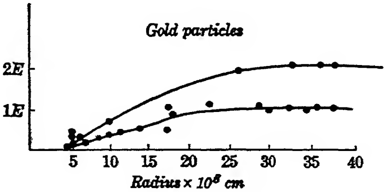

FIG. 19.

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[12] Zeitschr. f. Phys. 3, 63 (1920).

obtained for all particles of larger radii than 27×10^{-6} cm. Below this limiting radius deviations from the fundamental unit are observable with increasing drop in radius. Comparison of the curves shows that even for the smaller particles the respective charges, though not equal to the elemental quantum, are multiples of some smaller "quantum." Using Einstein's equation (which is independent of the radius) for calculating the charge, no marked or systematic deviation from Millikan's unit was observable. Radel accordingly concludes that no real evidence has been produced to prove the existence of "subelectrons." Paraffin oil and rosin were not investigated below their minimal radii, and did not exhibit any deviation from the normal charge for larger particles. Regener[13] assumes that small metal particles adsorb large quantities of atmosphere. The minute particles adsorb much more atmosphere, relative to their respective masses, than do the larger particles; in other words, the density of the adsorbed atmosphere increases with the density of the particles. As a consequence, the total density of the observed particle, which carries with it the absorbed gas, becomes smaller. Furthermore, the particles become enlarged by the adsorbed gas films. They consequently would offer a greater frictional resistance to the gravitational force exerted upon them, i.e., their rate of fall varies. Inasmuch as the rate of fall and the radius are employed in the evaluation of the unit charge according to Stokes' formula, it is obvious that this would be seriously affected. However, if Regener's corrective factor for adsorbed atmosphere is adopted, the values for ϵ for the minute particles used by Ehrenhaft may be brought close to that determined for larger particles by Millikan.

It has been remarked elsewhere that the validity of the Cunningham corrective factor $(1 + A(\lambda/a))$ is limited to such cases only where $\lambda < 0.4$. K. Wolter,[14] accordingly, has attempted a series of experiments to magnify the effect of densely adsorbed gas films upon small particles by de-

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[13] Berl. Akad. 1920, 632.

[14] Zeitschr. f. Phys. 6, 339 (1921).

termining their respective charges at increased pressures (1 to 9 atmospheres). An increased pressure would tend to make the free mean path so short that the Cunningham correction factor of Stokes' law will be reduced to a negligible quantity. Particles of smaller size (those that yield low results for ϵ, as in Ehrenhaft's and Radel's experiments) could thus be tested at higher pressures, where their mean free paths would be shorter. If the deviations in values observed by Ehrenhaft are attributed to size of the particle, they would diminish obviously under reduced pressure. The deviations observed at atmospheric pressure persisted also at higher pressures. No new deductions of an explanatory nature were forthcoming from these toilsome experiments largely because it was not possible to observe and measure the one and the same particle under various pressures. Yet it is noteworthy that, with an entirely different experimental procedure, Wolter should arrive at conclusions practically identical with those of Radel and find Stokes' law itself applicable. The recent work of M. König, likewise under Regener's guidance, is especially significant in this connection. As stated above, Radel found a constant value for the elemental charge associated with particles above a definite limiting radius. König investigated the downward deviations in mercury spherules in air and in CO_2; in accordance with greater absorbability of the carbon dioxide, the latter has a greater capacity to diminish density than has air even in the case of considerably larger particles.

Experiments of a very interesting nature were devised recently by Regener and Sanzenbacher. They develop the problem of the formation of adsorption films upon small particles according to a new method. It had been observed repeatedly that the mass of mercury droplets varied during the course of a single observation. Inasmuch as this change was invariably a decrease in mass, it was but natural to infer loss due to evaporation. On the other hand, other droplets, viewed simultaneously and treated similarly, did not give evidence of such variation. They accordingly proceeded to measure the elemental quantum charge of vaporizing and of non-vaporizing mercury droplets. In conformity with the aforementioned results of Radel and König no difference was found in the elemental charge of both type particles, provided they were of sufficiently large size. Not only were their respective charges alike but they proved equal also to the accepted Millikan value. With smaller droplets, however, the unit charge for "vaporizing" droplets no longer was equal to that of the "non-vaporizing" particle. Furthermore, the charge of the former type was found to be independent of its size, whereas the charge of the latter type deviated markedly, the deviation from the normal ϵ value being the more pronounced the smaller the radius. These results corroborate Ehrenhaft's contention. It was observed frequently, too, that a "vaporizing" mercury particle eventually became so small that it no longer was observable. Final measurements of the charge upon such vanishingly small droplets indicated always the same ϵ value which had been found for particles of larger sizes. It appears reasonable to assume, therefore, that the observed divergences in the magnitude of the electric quantum are not attributable to a difference in the electric charge, but are caused, rather, by the incorrect use of some material constants in the equations from which e is evaluated. It is highly probable that very small particles failing to vaporize are foreign substances, as, e.g., dust particles. Millikan has already pointed out, in his measurements on oil drops, the occasional abnormal behavior of small particles, which he considered to be dust particles. The experiments of Regener and Sanzenbacher indicate plainly, therefore, that evaporation is conditioned upon the pre-establishment of adsorption effects, inasmuch as the extent and the manner of evaporation progress to different extents in different gases. So long as "normal" evaporation persists the particle may be considered to be pure mercury. But when evaporation ceases, which happens very frequently in atmospheres of hydrogen, the surface of the droplet will no longer be a normal mercury surface because gas has been so strongly condensed upon it to prevent further evaporation. In the light of our present knowledge we are not in a position to decide whether the changes in the specific gravity or other effects that arise from the reciprocal action between the particle and the surrounding gas are the determining factors that become evident under such conditions.

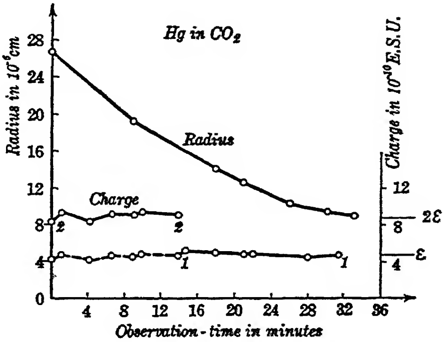

FIG. 20.

We shall cite two examples to demonstrate the vaporization process. Figure 20 depicts the data obtained for the vaporization of mercury in an atmosphere of carbon dioxide. Time of observation is designated along the abscissæ axis. The left ordinate indicates the radius of the particle whose decrease with elapse of time is graphed in the upper curve. The magnitude of the charge is measured along the right ordinate, the two lower curves showing the change in charge during evaporation. As is obvious, this remains constant even for the smallest particle of radius 8×10^{-6} cm.

The following Figure 21 shows a set of data obtained for the evaporation of mercury in air. Here it will be observed the radius at first increased, doubtless due to the addition of mercury vapor upon the particle under observation, and then a normal decrease set in. In this case also, with changing mass, the unit charge was constant and equal to the accepted Millikan value.

R. Bär[15] has elaborated, at the Zurich Institute (Edgar Meyer), a theory that contributes decisively to the eventual elucidation of this much disputed and perplexing problem "electron and subelectron." Bär's work is based essentially upon the investigations of Gerlach and Meyer, to which

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[15] Phys. Zeitschr. 22, 615 (1921).

reference has already been made. The Stokes-Cunningham law $K = 6\pi\mu av \dfrac{1}{1 + A\left(\dfrac{\lambda}{a}\right)}$ may be recast into the linear equation $v = \alpha + \beta\lambda$, in which form its accuracy may be tested experimentally by noting the velocity of fall of the same particle at various pressures (free mean path λ). Here

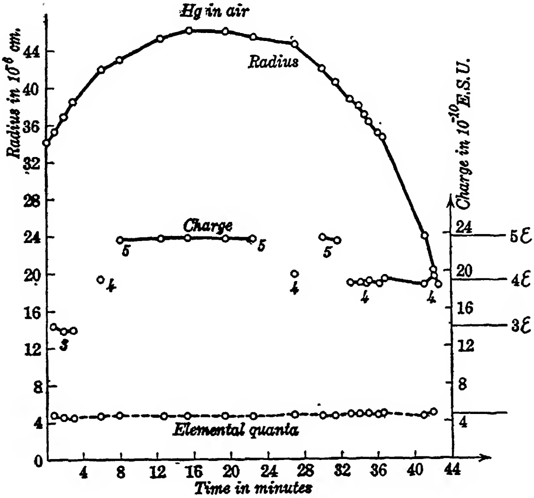

FIG. 21.

both α and β are constants whose values are functions of the radius of the particle; viz.: $\alpha = 2\sigma a^2 g/9\mu$ and $\beta = \dfrac{2\sigma a g}{9\mu} A$. On the other hand, β^2/α and A^2 are mutually so related that the ratio $\dfrac{\beta^2}{\alpha} = \dfrac{2g}{9\mu} \cdot A^2$ is independent of the radius and calculable for each material whose density σ and whose corrective factor A are known. Assuming the particle to be that of the compact parent material and making $A = .815$, there should result for the ratio $\beta^2/\alpha = C$ a characteristic constant C. Experimental measurements of the velocity of a particle falling in a gas medium under various pressures demonstrated, however, that this ratio was variable. The observed deviations from constancy in C values may be grouped in one of two classes. Thus, selenium particles evidenced, with decreasing size, a progressively greater deviation from the theoretically anticipated value of β^2/α. Obviously, the density of the particle cannot be greater than that of the original compact material. The inference is, therefore, that A, or in other words the validity of Stokes' law itself, has been wrongly assumed. As a matter of fact no linear dependence of v upon λ was detected, as is postulated above in $v = \alpha + \beta\lambda$. The experimental data pointed rather to the validity of the Knudsen-Weber law. This leads to other values for α and β (Fig. 22) with the use of which all differences of electronic charge vanish, while linear interpolation between points P_1 and P_2 would lead to false constants α' and β'. For platinum particles an entirely different behavior was noted. Here, the ratio β^2/α decreased with decreasing radius, dropping at times to one hundredth of its original value. Assuming the expression $\beta^2/\alpha = 1.2 \times 10^6 \cdot \sigma A^2$, it must be inferred that the specific gravity of

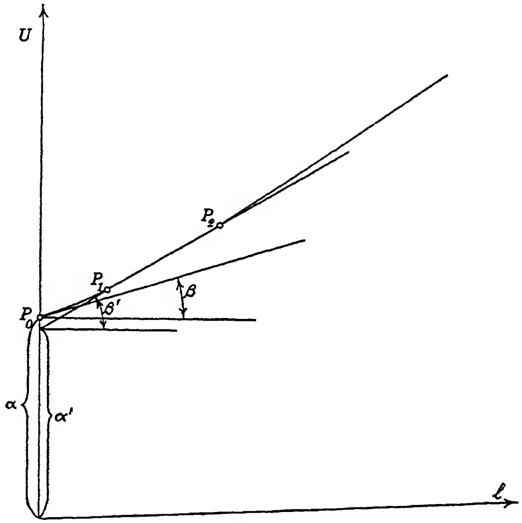

Fig. 22.

the particles has decreased to 1/100 of its normal value. All evidences of subelectrons vanish when the densities so determined for the various particles—from the "compact" material density 21 to the smallest value 0.2—are used to calculate the charges associated with the respective particles. It seems therefore that the inquiry into the existence of subelectronic charges may be closed with a definite negation, all the data presently available failing to establish its existence. Evidently, the true law of fall capable of reconciling these experimental divergencies is still unknown in its theoretical form. An empirical law, on the other hand, may be formulated if the velocity of fall of a given particle is measured as a function of the free path, i.e., of the pressure of the gas in which it is falling.

An example will serve to illustrate this point. Figure 22 represents the curve $P_0P_1P_2$, obtained when the velocity of fall v is measured as a function of λ. On the assumption of the linear law, $v = \alpha + \beta\lambda$ (Stokes-Cunningham), the incorrect values α' and β' may be obtained by linear interpolation from the measured values of P_1 and P_2. If we determine, on the other hand, the complete course of the curve $P_0P_1P_2$ and assume that the Stokes-Cunningham law is but a first approximation of the true law (Knudsen-Weber), the correct values α and β may be obtained by drawing the tangent at P_0. (A study of Figure 22 will make clear the differences of these corresponding correct and incorrect values.)

We shall make but passing reference to the experiments of Mattauch[16]—experiments which parallel those of R. Bär in purpose and in accomplishments.

We will now consider briefly the precision measurements of the elemental quantum which R. A. Millikan has carried out with steadily increased accuracy during the last twelve years. Figure 23 depicts the experimental arrangement

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[16] Zeitschr. f. Physik, 1925. These problems are treated in detail in the chapter on "electron" in the "Handbuch für Physik," vol. 22, 1926 (published by J. Springer, Berlin).

finally adopted by Milliken, the so-called oil-drop method. *MM* are parallel metallic condenser plates set in a rather wide chamber *D* which is evacuated or filled with an indifferent gas. This vessel, in turn, is placed in a thermostat. The material, the charge upon whose particles is to be ascertained (usually oil droplets), is sprayed into the chamber through the atomizer *A*. As the finely divided droplets, about one ten thousandth of an inch in diameter, slowly fall through the chamber, one will eventually find its egress through the small opening at *P* into the air space between the condenser plates. Here it is made visible as a bright speck by reflecting the light which is projected laterally into the condenser space by means of an arc lamp *a*, as shown at the left of the diagram. *w* and *d* are filters for the removal of the heat rays. As soon as a droplet has entered the condenser field, the minute aperture *P* is closed. The confined gas is then ionized by X-rays projected through the lateral opening on the right, this being done only when it is desired to vary the charge of the droplet. A known electrical potential is then impressed upon the plates *MM* by the battery *B*, so controlled by switches as to permit reversal of the charges on the upper and lower plates respectively. The condenser plates were plane

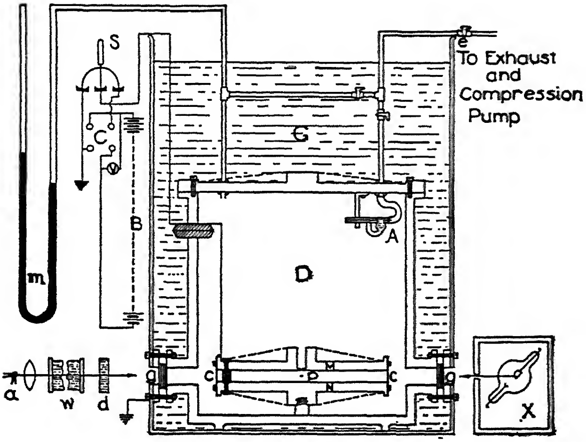

FIG. 23.

and highly polished and of diameter 22 cm. and separated from one another by means of three small glass plates of perfect parallelity and 14.9174 mm. thick. The droplets may assume a charge when they are sprayed from the atomizer *A* or they may become charged as a result of impact with ions in the condenser space. With the condenser plates uncharged, the confined droplet was observed to fall with a slow and measurable speed (about 1/13 inch per sec.), which could be altered by impressing upon the plates a definite potential from *B*. The speed in each case would be governed by the sign of the charge of the droplet and that of the upper plate. When these are alike, the droplet falls rapidly. By reversal of the sign of the charge, the direction of the velocity would be reversed, thus producing a rise. By alternating the charge upon the upper plate, therefore, the droplet may be made to migrate up and down between the plates. Obviously a rise against gravity will result only when the potential applied to the upper plate exceeds the gravitational influence upon the droplet. Mere neutralization of gravity effects would keep the droplet at rest and suspended between the plates. During its up and down excursions the droplet may collide eventually with one or more ions sent in the gas, thus altering its electrical condition. When rising against gravity, therefore, under the influence of a definite electrical field, the required time of rise will vary, depending upon the extent of the variation in its charge. With uncharged plates, on the other hand, its rate of fall will remain constant. The extent to which the droplet will assume ions (corresponding to an increase, neutralization or reversal of its initial charge) will thus be indicated by the variation in the velocity of rise. If electricity is atomic or granular in nature, the variations in the rising velocities should evidence a definite relationship to one another, expressing in any one case a velocity which will be a multiple of some minimum velocity, the latter corresponding to the velocity due to the presence of the unit or elemental charge upon the droplet. Such results were achieved by Millikan, thereby establishing proof of the existence of the electron. Inasmuch as the potential impressed upon the condenser was measurable with an accuracy of 1 to 3,000, the field intensity may be ascertained readily with great precision. In connection with these experiments, the coefficients of friction μ of gaseous media have been frequently determined by Millikan, Gildchrist, Harrington. The accepted value for dry air at 23 degrees (= .0001824) needed correction by only .1 per cent to .00018227. The velocity of fall of the particles, which is necessary to determine the mass according to the law of fall, were computed from measurements of the time of fall, which were registered by recording chronographs to 1/100 second, for a total falling interval of 14 to 60 sec. and a distance of 1.0220 cm. (accuracy 1 to 2,000). The specific gravity of the oil was 0.9199 at 23° C.

Little has been said thus far concerning the Cunningham corrective factor

$$C = \frac{1}{1 + A\dfrac{1}{pa}}.$$

Its magnitude was determined experimentally by Millikan. To accomplish this, the radius a of the particle, as well as the pressure p of the gas in which it is falling, is made to vary. According to the formulæ already quoted,

$$mg = 6\pi\mu avC = \tfrac{4}{3}\pi a^3\sigma g = \epsilon E,$$

$$\alpha^2 = \frac{9\mu v}{2\sigma g}\cdot C,$$

$$\epsilon^{2/3} = \frac{9\sqrt[3]{\dfrac{2}{9}}\cdot\pi^{2/3}}{E^{2/3}\sigma^{1/3}g^{1/3}}\,\mu v\cdot C.$$

Let us designate the right hand member of the equation by $\epsilon_1^{2/3}C$, where ϵ_1 represents the uncorrected elemental quantum as obtained from the directly measured factors contained in the fraction. If the correction is of the form

$(1 + A(\lambda/a))^{-1}$ (or in place of λ/a we may put $1/pa$), it follows that $\epsilon_1{}^{2/3} = \epsilon^{2/3} + A\epsilon^{2/3} \cdot 1/pa$.

In other words, the $\epsilon_1{}^{2/3}$ values, measured as functions of $1/pa$, must lie on a straight line for all values of pa, which line for $1/pa = 0$ passes through the ordinate $\epsilon^{2/3}$, thus to the corrected value. This anticipated value was fully realized in all cases. Figure 24 shows a typical instance.

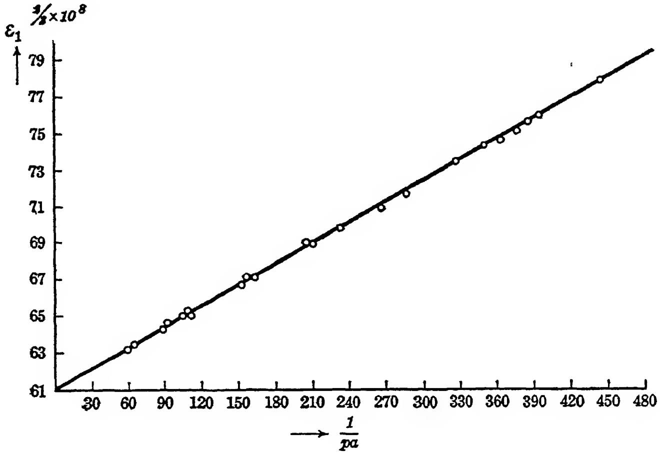

Fig. 24.

Invariably particles of the same type falling in the same gas yield such a straight line. The measurements were therefore restricted to such ranges in which a linear relationship still persisted for A and λ. If either the material of the particle or the gaseous medium be changed, a linear function still obtains but this has a different slope. We may express this in more general terms, viz.: a linear relationship is evident for all cases, each material and each gas yielding a line of definite slope, that is, of different A values. The Cunningham factor evidently is dependent upon these two experimental factors, material of particle and gaseous medium in which the former is permitted to fall. It is interesting to note, in this regard, that all these straight lines, expressive as they are of the mutual dependence of particle and gas, intersected the

$\epsilon_1^{2/3}$ ordinate at the one and the same point, viz.: the corrected ϵ value. In electrostatic units, this common intersection point may be expressed as

$$\boxed{\epsilon = (4.774 \pm 0.0005) \times 10^{-10}.}$$

It is possible also by means of this partly graphic and partly experimental method of Millikan to evaluate the constant A. Using the data made available by these experiments, Millikan calculated the following values:

$$A = \left[\left(\frac{\epsilon_1}{\epsilon}\right)^{2/3} - 1\right] \cdot pa.$$

For:

Oil droplets in air	0.875
Oil droplets in hydrogen	0.811
Mercury particles in air	0.711
Theoretical maximum	1.630
Theoretical minimum	0.815

It was observed that this "constant" was not entirely independent of the relative free path radius of particles, if this was permitted to vary within wide ranges. It appears preferable, accordingly, to express the law of fall in a more comprehensive formulation, somewhat as

$$mg = 6\pi\mu av\{1 + A(0.864 + 0.29e^{-1.25(pa/A)})1/pa\}^{-1},$$

for all values of A between 0.804 and 1.39. Millikan's empirical law may be formulated as

$$mg = 6\pi\mu av\{1 + (0.864 + 0.29e^{-1.25pa})1/pa\}^{-1},$$

which is in accord with the law of Knudsen and Weber, when $A = 1$.

The following table contains a résumé, as compiled by R. Bär, of the A' values of Cunningham's corrective factor. The free path has been calculated by means of the formula for internal friction $\mu = 1.3502n \cdot m\bar{c}l$.

We may conclude from the data presented that a determination of the elemental quantum necessarily involves a knowledge of the appropriate law of fall applicable to each case. Theoretical prejudice and injudicious considerations and deductions drawn from the available experimental data invariably will lead the unwary to the concept of "subelectron."

Author	Experimental Material	*A*-value	Literature
E. Cunningham....	Theory	0.857–1.71	Proc. Roy. Soc. A. 83, 357 (1910).
Zerner............	Theory	1.40 –1.58	Physik. Zeitschr. 20, 546 (1919).
Lenard............	Theory	0.948–1.58	Ann. d. Phys. 60, 329 (1919).
Knudsen and Weber..........	Glass spherules in air	$0.772 + 0.40e^{-1.633(a/\lambda)}$	Ann. d. Phys. 36, 981 (1911).
McKeehan........	Wax particles in air	1.05	Physik. Zeitschr. 12, 707 (1911).
McKeehan........	Shellac particles in air	1.07	Phys. Rev. 4, 420 (1914).
Millikan, Barber and Ishida.......	Oil droplets in hydrogen	0.820	Phys. Rev. 5, 334 (1915).
Schidlof and Murzinowska....	Oil droplets in air	0.882	Arch. d. Gen. 40, Nov.-Dec. (1915).
Schidlof and Karpowicz.......	Mercury particles in air	0.882	Arch. d. Gen. 41 (1916).
Silvey.............	Mercury particles in air	0.886 and 1.03	Phys. Rev. 7, 87 (1916).
Targonski.........	Mercury particles in air	0.878	Arch. d. Gen. 41 (1916).
Derieux...........	Mercury particles in air	0.695	Phys. Rev. 11, 203 (1918).
Millikan...........	Oil droplets in air	$0.864 + 0.29e^{-1.25(a/\lambda)}$	Phys. Rev. 15, 544 (1920).
Lassalle...........	Oil droplets in carbon dioxide	0.825	Phys. Rev. 18, 98 (1921).

A theoretical calculation of the elemental quantum of electricity, remarkable for its accuracy and definiteness, is based upon the Rydberg constant N of the formula for spectral series, a constant theoretically explained by Bohr and experimentally determined by Paschen. This constant, as we now know (Chap. XII), designates the ultra-violet limit of the H-spectrum (Lyman-series limit). Its magnitude —given as the number of vibrations of the H-spectrum limit— is 3.291×10^{15} sec.$^{-1}$. Its theoretical derivation, based upon Bohr's theory of atomic structure, leads to the formula,

$$N = \frac{2\pi^2\epsilon^4\mu}{h^3},$$

in which ϵ and μ designate respectively the elemental quantum and its mass and h is the Planck constant. Substituting the known values, we obtain the result: $N = 3.291 \times 10^{15}$ sec.$^{-1}$; which is a remarkable agreement with that obtained from observations on spectral series. N may be considered as very definitely evaluated experimentally. In addition there are known rather accurately the ratio ϵ/μ, the specific charge of an electron ($= 5.35 \times 10^{17}$ E.S.U.), and the ratio h/ϵ ($= 1.36 \times 10^{-17}$) which is directly determinable from photo-electric measurements and stimulation by X-rays. The above equation may consequently be formulated as

$$N = \frac{2\pi^2\epsilon^2}{\left(\frac{\epsilon}{\mu}\right)\left(\frac{h}{\epsilon}\right)^3} = 3.291 \times 10^{15},$$

from which, after substitution of the proper magnitudes, ϵ is obtained equal to 4.8×10^{-10} E.S.U., a perfect agreement with Millikan's experimentally measured value.

If we now recall the value previously found for the ratio charge/mass and combine this value with that of ϵ as determined by Millikan, we may evaluate the mass of an electron to be

$$\mu = 8.996 \times 10^{-28} \text{ grams.}$$

Its "atomic weight" obviously is 1/1,833 that of hydrogen. It should be recalled that this mass is the so-called "rest mass," i.e., the mass of such electrons as are moving rather slowly with respect to the velocity of light. For mass is a function of velocity. The classical experiments of Kaufman corroborated by experiments of Bucherer, Neumann, Guye et al., which deal with the variation of mass of cathode rays as a function of velocity, demonstrate conclusively that mass increases with velocity. Such a dependence is likewise a consequence of the relativity theory. This phenomenon is confirmed further by the application of Sommerfield's relativity correction in the theory of line spectra to Paschen's measurements. We will not enter into this phase of the subject matter.[17]

It may be remarked at this point that in no scientific dispute within the realms of physics does there seem to have been available so much experimental material and data than in this controversy about the existence of the electron. It was stated in a previous section that the existence of an elemental quantum is accepted as very definitely proven. We may also accept, without any great chance of error, its magnitude as lying very close to the value obtained for it by Millikan, even though there is a possibility that the accuracy (1 per 1,000) claimed by Millikan for his results has been judged a trifle optimistically. A much more serious problem is presented, however, when we review the results of experiments which to all indications are similar in scope and purpose. We refer to those experiments whose data furnish evidence of a subquantum, a subelectron. But why should similarly planned researches sometimes prove the existence of an elementary electrical unit, and at other times a submultiple of it? To attempt a decisive answer to this difficult problem would be banal. All that one may safely claim is not so much a possibility of difference in charge, but rather an indication of our ignorance concerning the hydrodynamic and gas-kinetic behavior of very small particles moving with friction in various media. Added to this, the form and the physical condition of such small particles is unknown and may not be investigated directly. We may readily conceive, therefore, how Bär arrived at the assumption of abnormally

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[17] A. Landé, Wissenschaftliche Forschungsberichte, 4.

small specific gravities as the result of the sponge-like structure of minute particles; it is likewise easily intelligible how Regener attributed too small densities to gas adsorption. Recently, L. Schiller suggested that deviations from the spherical form are a contributing factor and may explain and account for these differences. His assumptions appear too arbitrary but it is impossible to proceed for the present without the aid of assumptions. As a consequence, we must content ourselves with our present limitations and acknowledge our inability to present adequate reasons for these differences in experimental data. Without a doubt, there are very many reasons, each of which is a contributing factor to this apparent inconsistency.

CHAPTER VII

THE SPECIFIC CHARGE OF THE ELECTRON: ϵ/μ_0

In the previous chapter we discussed the determination of the charge upon the electron. We saw that a variation in the charge of the elemental unit, i.e., the electron, was very easily detectable by disturbing the equilibrium of a particle suspended in a condenser. The question now arises, are we in a position, likewise, to make a definite statement concerning the mass of the electron; for example, does the particle under observation simultaneously become lighter while sustaining a loss of charge? Such a mass variation has hitherto not been observed, although there are a number of other indications which suggest that the mass of an electron must be smaller even than the mass of the hydrogen atom. On the other hand, the measurement of "atomic masses" is not possible with any of our hitherto devised scales. Moreover, the suspended particle eludes our present methods of measurements. From the relationship $mg = eE$, we obtain the variation $\delta m/m = \delta E/E$; in other words, the smallest demonstrable mass variation may be obtained from $\delta m = m \times \delta E/E$. If E is measurable to 0.1 per cent—whereby $\delta E/E = 10^{-3}$—for a particle of radius $= 10^{-6}$ cm. (very small droplets) and for a material of specific gravity $= 1$, the mass variation will thus become $\delta m = 4 \times 10^{-20}$g. This means that the smallest demonstrable mass change, under these conditions, would be equivalent to the mass of about 40,000 hydrogen atoms or about 200 mercury atoms.

Obviously, methods suitable for the determination of "gravity mass" are not applicable to the determination of the mass of an electron. We must have recourse, rather, to the methods of determining inertial mass. The fundamentals of the several methods applicable in this respect have already been discussed in Chapter II (Isotopy) in our considerations of the mass spectra of positive rays. If the method suggested there for the measurement of the relation: charge to mass, be applied to ions of the most varied types, an abnormally great value will be found under certain conditions, a value approximately 2,000 greater than that obtained for the positive ion from hydrogen atoms. This extreme value is found only for ions of negative sign, and was first observed in investigations of cathode rays. Accordingly, the conclusion was drawn (it was Wischert who first expressed this clearly and concisely) that the mass of the charged particles in motion constituting the cathode ray must be 2,000 times smaller than the lightest of our known material ions.

The mass determination of the electron is conditioned, therefore, upon the determination of the electronic charge and of the specific charge of the electron. Since these involve measurements of electrons in motion, it will be necessary briefly to consider the laws of motion as applied to electrons. Let us assume an electron at rest between two metallic plates. If an electric field is impressed upon these plates, the electron will be accelerated. If E is the intensity of the impressed field, and ϵ the electronic charge, the electron, after traversing a distance l, will possess a velocity v, in the direction of the electric field, which may be evaluated from the energy equation $\frac{1}{2}mv^2 = \epsilon El = \epsilon V$. Here V is the potential difference in volts. Let the electron now enter, with this velocity, v, into the confines of an electric field E' whose lines of force are perpendicular to the motion of the electron. A continuous force immediately will act upon the electron perpendicular to its direction, whereby it will experience an acceleration in the direction of these lines of force, at the same time retaining its initial constant velocity. The path traced by the electron will thus correspond to the well-known parabolic form of projectile motion. The deflection from its initial course, i.e., its motion in the direction of the transverse field, is calculable from the general equation of falling bodies, $S = \frac{1}{2}bt^2 = \epsilon E'/2\mu \cdot t^2$. Here E' designates the transverse field, t the time during which the electron traverses the field, and ϵ/μ the specific charge, which becomes readily calculable when the other magnitudes are known.

The electron will likewise suffer a change in direction in a transverse magnetic field, H, i.e., a field whose lines of force run perpendicular to the direction of the electron. According to well-known electromagnetic laws this change is such that the direction of the electron continuously remains perpendicular to the direction of the magnetic force lines. The bending or deflecting force is equal to ϵvH and is constant, as a result of which the electron will describe a circular path in the magnetic field about the lines of force. At equilibrium this force equals the centrifugal force of the moving particle acting outward along its radius of curvature. Or $\epsilon vH = v^2/r$, from which $r = v/\epsilon H$. Since r and H are both measurable, we have here again a relationship from which (if the electron enters the field with a known velocity v) the specific charge ϵ/μ may be evaluated. At this point we will not discuss the numerous experimental methods[1] which have been devised for the determination of the specific charge; we shall content ourselves with a table of all the more probably trustworthy values, citing all the measurements made. Later we shall discuss, merely as an example, one of these methods more in detail. It is important to remark, in passing, that the specific charge of the electron has been found always to have the same value, no matter in what manner it may have been produced. Most diversified methods were utilized to establish this fact. Attention has been drawn elsewhere to the investigations of the cathode rays arising in vacuum tubes. In a similar manner electron rays arising from a Wehnelt electrode (Oxydkathode) or from thermionic electrodes (Richardson electrodes) were applied to the solution of this problem. In addition, methods were devised involving the use of photo-electric electrons ejected from metals by ultraviolet light or by X-rays; and finally we have pressed into service, for the determination of the specific charge of the

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[1] For details see W. Gerlach, chapter on electrons in volume 22 (Handbuch der Physik, Geiger-Scheel., Berlin, 1926).

Compilation of All ϵ/μ_0 Measurements

Method	Author	Result ($\times 10^{-7}$) Electromagnetic Units	Remarks
β-rays	H. Becquerel	order = 1	Attempt to determine nature of β-rays.
β-rays Simultaneous deflection in crossed elect. and mag. fields	W. Kaufman, 1901, 1902	$\epsilon/\mu_0 = 1.84$ 1.77	— —
	1906	according to Abraham = 1.823 according to Lorentz = 1.660	Deviation of the results of these two theories is greater than the accuracy of measurement.
β-rays Electric and magnetic compensation; magnetic deflection	A. H. Bucherer, 1909	according to Lorentz = 1.766 ± ½% according to Abraham = 1.711	β-range 0.3–0.5.
	K. Wolz, 1909	according to Lorentz = 1.770 ± ½%	β-range 0.5–0.7.
	Neumann-Schaefer, 1914, 1916	according to Lorentz = 1.767 ± ⅕%	β-range 0.35–0.85, very good confirmation of Lorentz-Einstein dependence on mass.
Zeeman-Effect	Gmelin	1.770 ± 0.005	—
	Fortrat	1.763 ± 0.003	—
Spectroscopically from Rydberg constant for hydrogen and helium	Paschen (exp.) Bohr-Sommerfeld (theoretically)	1.7686 ± 0.003	Newly calculated for helium atomic weight of 4.001 ± 0.0017.
Photo-electric electrons	E. Alberti, 1912	(1.756) 1.766	Number in parenthesis obtained without field correction.
Oxydelectrons	J. Classen, 1908	1.773 ± 0.004	1,000 and 4,000 volt-rays.
Oxydelectrons	A. Bestelmeyer, 1911	1.766	870 = volt-rays.
Slow cathode rays	M. Malassez, 1911	1.769	$\beta = 0.26$.

electron, the β-rays of various velocities, emitted from radioactive substances.

For completeness' sake, it may be remarked that the specific charge has been determined not only for free electrons (i.e., atoms of electricity that may be released from matter by means of any of the methods specified above) but also for electrons "bound" within the atom. These are susceptible to experimentation by noting the changes which their orbits (and consequently the radiation changes depending upon their orbits, i.e., spectral line emissions) undergo in a magnetic field. This phenomenon, known as the Zeeman-Effect, which is essentially a splitting of the spectral lines due to the influence of the magnetic field, has been explained by H. A. Lorentz by postulating a precession of movement of electrons in definite orbits about the direction of the magnetic field. Here again do we find that the relation of electronic charge to mass occurs as a characteristic factor.

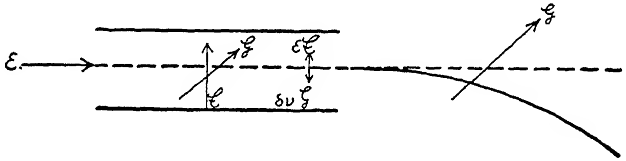

FIG. 25.

We shall discuss more completely the method first elaborated by Bucherer and subsequently improved experimentally, especially by Neumann and Schaefer, and which is founded, in principle, upon a consideration proposed as early as 1900 by W. Wien. Examination of the above-mentioned formulæ for determining the deviation of cathode rays in electric and magnetic fields will show, for cathode rays of a definite velocity, that there must be a fixed position and intensity of both fields, relative to the direction of the electron, for which the electric and magnetic deviations compensate each other exactly. Suppose an electric field operative in a condenser in an upward direction (Fig. 25) upon an electron moving initially in a left-to-right direction. At the same time, let a magnetic field be established in a direction perpendicular to the lines of force of the condenser and likewise perpendicular to the plane of the paper. Under such conditions the path of the electron will be deflected upward by the electrostatic influence and downward by the magnetic field. For simultaneous operation of both fields, the net deviation will become zero if the following condition is fulfilled, viz.: if $\epsilon E' = \epsilon vH$. Obviously, cathode rays possessing a velocity of $v = E'/H$ will emerge from the condenser in the same direction in which they had entered it, whereas all other electrons are deviated from their initial direction either upward or downward depending upon their respective velocities. Upon emergence, therefore, the cathode stream will consist only of electrons of uniform and known velocity. If this uniform ray is now subjected to the influence of a magnetic field only, it will experience a deflection $\rho = 1/R$ which is derivable from the relation $\mu v^2 \rho = \epsilon vH$ and which leads directly to the calculable value of the specific charge of the electron

$$\epsilon/\mu = \rho v/H = \rho \cdot E'/H^2,$$

since $v = E'/H$. It is apparent, therefore, that this method yields not only the specific charge, but it indicates, likewise, the dependence of the specific charge upon velocity. In other words, if the charge is considered independent of the velocity, it designates the dependence of mass upon velocity.

The performance of the experiments entails a series of very difficult correction factors, since it is not possible sharply to confine electric and magnetic fields within definite spatial limits. These sources of error were overcome fairly well, especially by Neumann. β-rays from radium with a velocity range of 0.3 to .86 that of light were utilized as source of cathode rays. In addition to furnishing a very reliable value for the specific charge, the data confirmed likewise the relativistic dependence of mass upon velocity.

CHAPTER VIII

THE MAGNETON

As we have seen from the two foregoing chapters, we possess a very complete knowledge of the nature of the electric charge. Not only do we know the magnitude of the unit electric charge, the electron, and its mass, but we know likewise that all electrical phenomena are attributable to the presence of moving electrons or to electrons at rest. Because of the close analogy which exists between the laws of electric and magnetic behaviors, it is most reasonable to inquire whether phenomena of a magnetic character may be explained in a like manner, i.e., by postulating the presence of units of magnetism either at rest or in motion. Consideration of even the simplest magnetic phenomena, however, indicates that the existing analogy between electric and magnetic fields does not extend to the sources of their respective lines of force. For, while it is within our power to charge, at will, any body either electro-positively or electro-negatively, we have not yet succeeded in producing a body, or so influencing a body, as to impose upon it a charge of either positive or negative magnetism only. Furthermore, each magnet consists of two equally strong poles of opposite signs. While, therefore, the electric lines of force may originate in one body and terminate in another, both source and terminus of the magnetic lines of force are situated within the one and the same body. Stated differently, this means that there are no free magnetic charges and that the magnetic character of a body results only from its polarization.

Precisely this consideration of polarization has made it possible to regard magnetism not as a new phenomenon but rather to correlate it with another phenomenon, viz.: the electric current. A wire coil through which a current is flowing displays those very characteristics which are peculiar to a magnet: closed magnetic lines of force arising at one side of the coil proceed through the air in a circular fashion and terminate on the other face of the loop. It was proposed, therefore, to explain magnetic phenomena in the light of the phenomena observable in the neighborhood of a current-bearing loop. Theories, expressive of such a relationship, have been propounded by Ampere and by Weber. Ampere assumes that the analogy between a magnet and a current-bearing loop pertains not merely to their external similarities but that electric currents of fixed direction are present within the magnet as a consequence of which its exterior magnetic field is produced. Ampere's molecular current theory, therefore, advances the hypothesis (as is indicated by its name) that in each molecule of a magnetic substance there is an electric current flowing in a fixed channel. Should these currents have unorganized directions, the body in question is exteriorly non-magnetic. If, however, a considerable number of these current channels are mutually parallel, the body will exhibit an exterior magnetic moment. It is evident that we may formulate, upon these assumptions, more or less crudely, a notion regarding the manner in which a magnetic substance becomes magnetized. This is especially remarkable as it may be accomplished with ideas that are particularly familiar nowadays. It is apparent, also, that not every material is capable of being thus magnetized since magnetization presupposes the existence of molecular current channels. Although this hypothesis thus affords a ready explanation for certain phenomena, nevertheless it is beset by one great difficulty. It is a very well-known fact that permanent magnets may be prepared which retain for appreciable lengths of time their magnetic moment when kept with appropriate care. Such a phenomenon necessitates a continuously constant value for the molecular currents begetting the magnetic character. Expressed in electrical terms, the channels, through which these molecular currents flow, ought to be non-resistant (perfect) conductors.

The modern theory of the atom postulates the existence of such molecular currents as a basis for the theory of atomic structure. According to it, electrons are in motion within the atom in closed orbits. Even though the more recent developments in the atom theory have engendered doubt as to the physical reality of such revolving electrons or at least as regards the mechanical explanation of such motion, we shall nevertheless retain unreservedly the usual representation for the following discussions, perhaps not entirely without great justification. For, precisely the magnetic phenomena, which we are about to consider, can be regarded, even now, as direct evidence of the existence of such electronic orbits, i.e., molecular currents, all other thought to the contrary. Before we undertake to deduce the magnetic properties of an atom from the simplest assumptions of Bohr's theory, it will behoove us to introduce a concept which will serve us to advantage in characterizing the magnetic constant of an atom, viz.: the concept of the elementary magnetic moment.

As the electron is the atomistic moment of electricity, we shall adopt the effect of the revolving electron as the atomistic moment of magnetism; and as the electron is an atomic being, the "magneton" is an atomic property. Nevertheless the concept "magneton" is derivable in somewhat similar manner as the concept "atom" was formed as the smallest self-subsisting structural unit of matter, viz.: by means of a mental operation of subdivision carried out until the ultimate limit of division has been reached. Let us take a magnet of pole strength m and length l. This will be characterized by its magnetic moment $M = m \cdot l$. If this magnet be cut into smaller sections, perpendicular to its axis, a number of magnets will be obtained, all possessing the same pole strength m, but smaller moments, viz.: $m\lambda_1$, $m\lambda_2$, $m\lambda_3$, $\cdots$, where λ_1, λ_2, λ_3, etc., designate the lengths of the several sections. For the summation of all these smaller magnets we have

$$\Sigma m\lambda_1 = m\Sigma\lambda_1 = ml = M.$$

On the other hand, if the magnet be divided into smaller fragments along the direction of its length, the several sections all will possess the same length l as the original magnet but different pole strengths. The moments of the magnets thus obtained are $\mu_1 l$, $\mu_2 l$, $\mu_3 l$, etc. Or

$$\Sigma\mu_1 l = l\Sigma\mu_1 = lm = M.$$

We can conceive such a subdivision carried out progressively until the dimensions of the sections—lengthwise and crosswise—will be those of the individual atoms. Magnets will thus result which may be designated "atomic magnets" or "elemental magnets" having an "atomic moment." It must be added, here, that such a subdivision of a magnet is meaningless physically, since the "elemental magnets" of an iron bar cannot be the atoms themselves. However, we shall not enter into a fuller discussion of this problem at this point.

Let us rather turn our attention to the consideration of any atom at all, entirely disregarding its ferromagnetic properties or even the para- or diamagnetic behavior of matter. As noted above, according to the modern atom theory as established by Rutherford, molecular currents are present in every atom, each of which represents a magnetic moment. We may thus choose for discussion the simplest case, viz.: the hydrogen atom, and we shall assume that this consists of a more or less heavy mass-nucleus with a positive charge and a light electron revolving about the nucleus at a distance a. In the light of this definitely established viewpoint, Ampere's theory of molecular currents has been set upon a real atomistic basis. Bohr has shown how a numerical estimate of the magnetic moment of such an atom may be arrived at in a very simple manner. In a subsequent chapter we shall see how Bohr calculated, on the basis of this model, the wave-lengths of the spectral lines emitted by hydrogen atoms. The calculation of the magnetic moment is similar in many respects to this calculation. An hydrogen atom, comprised of the constituents mentioned above, mechanically is similar to a rotator whose mechanical moment of momentum is derivable from the mass of the revolving electron μ, its orbital radius a, and the angular velocity ω, according to the following equation

$$J = \omega\mu a^2.$$

From the same magnitudes, substituting only the charge of the electron ϵ for its mass μ, the magnetic moment of the circular current produced by the rotating electron may be determined from the equation,

$$m = \epsilon \cdot \omega/2\pi \cdot \pi a^2,$$

in which the factor $\omega/2\pi$ is the number of revolutions made per unit time and πa^2 the circumscribed surface. Evidently, also, m and J are related as

$$m = \tfrac{1}{2}\epsilon/\mu \cdot J.$$

The moment of the momentum is further conditioned upon a definite requirement postulated by the Quantum theory: the moment of the momentum is equal to $h/2\pi$, or to some whole multiple of it, as $n \cdot h/2\pi$ $(n = 1, 2, 3, \cdots)$, where h is the so-called Planck constant (see Chap. XII). Or $m = \frac{1}{2}\epsilon/\mu \cdot nh/2\pi = \epsilon/\mu \cdot nh/4$. Taking $n = 1$, $m = \epsilon/\mu \cdot h/4$. Thus, to determine the numerical value of the magnetic moment m, all that is needed is the ratio of ϵ/μ, the specific charge, and Planck's constant. Substituting these respective values, $\epsilon/\mu = 1.77 \times 10^7$ and $h = 6.53 \times 10^{-27}$, we obtain for m the value, $m = 9.21 \times 10^{-21}$ gaus. cm.^{3}.

A fact to be noted regarding the equation just derived is the absence in it of special constants characteristic of the atom in question, e.g., its nuclear charge or the radius of the electronic orbit. Obviously, m, as so derived, is independent of any particular atom. This universal magnetic unit is termed "Bohr's magneton." It may be assumed, therefore, and with reason, that for higher atoms with a greater number of electrons, each individual electron generates such a current of equal magnetic moment. But since the direction of the electronic orbits of two revolving electrons may be opposed to each other, i.e., one may rotate right-handedly, while the other left-handedly about the nucleus, and since in addition the planes of the orbits may be inclined to each other, a complex atom with several electrons need not of necessity possess more than one magneton unit. Indeed, the effects of the individual moments of the various electrons can neutralize one another exteriorly, and, as far as our present knowledge of the magnetic moment of individual atoms is concerned, it is altogether likely that they occur in pairs, the orbits running counter to one another, as a consequence of which an atom with an even number of electrons within its structure may not give evidence of a magnetic moment exteriorly. Accordingly, if we identify Ampere's "molecular currents" with the orderly movement of the electrons within the atom, we are in a position to co-relate and bring into closer accord the various fundamental principles of our atom theories; but we do not solve thereby the very perplexing problem cited above regarding the source of energy which makes possible a constancy in the molecular current. It fails to explain why the molecular current proceeds unresistedly. On classical electromagnetic theory, a presentation of such molecular current is absolutely not possible since the moving electron must loose energy while emitting radiations. However, we will not attempt to advance a new hypothesis, for we recognize here the perplexity which permeates all our atom theories and which in the final analysis leads to the question of the permanence of the atoms. But now that the permanence of the atom has been proved by experience, we must accept this difficulty so long as we wish—and are able—to explain the electrical and magnetic reaction in the atom on the above-mentioned mechanical basis, and so long as the accepted mechanism agrees with experiment and is of such heuristic utility as that adopted here.

With regard to the more recent developments in the theory of the magneton we shall merely state here that these ascribe a magnetic moment to the electron itself. This new hypothesis of the rotating electron, however, as advanced by Goudsmit and Uhlenbeck, presents advantages only in the unification of the theoretical speculations. No experiment has as yet been published as a test for this theory; likewise no finding that would require a magnetic moment on the part of the electron.

We may now ask: what will happen if a "free" atom having a magnetic moment is brought into a magnetic field? The atom would immediately set itself so that the direction of its moment axis conforms to the direction of the lines of force of the field. This orientation need not affect the entire atom for it will suffice if the electronic orbit producing the moment so adjusts itself that its plane will be perpendicular to the direction of the force lines. If the field be inhomogeneous, the atom will be subject likewise to a ponderomotive force whose magnitude will be dependent upon the product of the magnetic moment of the atom and the inhomogeneity. It thus becomes possible to ascertain the moment of an atom if its deflection is capable of measurement. Such a procedure is quite feasible [1] and in fact has been undertaken by Gerlach and Stern. Suppose an atomic ray (see Chap. III) of silver produced by vaporizing the metal in a very high vacuum is brought through an inhomogeneous magnetic field, so constituted that its direction is parallel to the direction of the inhomogeneity. Under such conditions, atoms orientated in the direction of the field will be deflected from their path in the same direction, the atomic ray proceeding perpendicular to the direction of the lines of force. The extent of the deflection is derivable by means of a simple calculation which is closely analogous to the calculation of the deviation experienced by cathode rays in an electrostatic field which was discussed in the foregoing Chapter VII.

If we designate by $\delta H/\delta s$ the inhomogeneity of the field whose direction coincides with that of the field, there will be operative, upon an atom of moment m, a force K, so that

$$K = m \cdot \delta H/\delta s,$$

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[1] Literature: O. Stern, Zeitschr. f. Physik, 7, 249 (1921); W. Gerlach and O. Stern, Ann. d. Phys. 74, 673 (1924); W. Gerlach, Ann. d. Phys. 76, 163 (1925); also, W. Gerlach, vol. 2 of "Ergebnisse der exacten Naturwissenschaften" published by J. Springer, 1923.

which obviously is independent of the field intensity H. This force K will impart to the atom an acceleration

$$b = K/\mu = m\delta H/\mu\delta s.$$

The atom accordingly will penetrate the inhomogeneous magnetic field produced by a wedge-shaped pole-piece of a powerful electromagnet with a velocity $v = l/t$, where l is the length of the pole-piece. Figure 26 shows a cross section through the wedge-shaped pole, the arrow indicating the direction of H and of $-\delta H/\delta s$, while A represents an atom moving rapidly in a direction parallel to S and consequently perpendicularly to the plane of the diagram. The deviation from its path experienced by the atom under these conditions is, therefore,

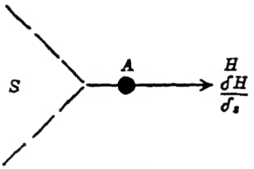


FIG. 26.

$$s = \tfrac{1}{2}bt^2 = \tfrac{1}{2}\cdot b\cdot l^2/v^2 = \tfrac{1}{2}m/\mu\cdot\delta H/\delta s\cdot l^2/v^2.$$

In this expression all magnitudes except m are measurable; that is, m is ascertainable provided there be available a method to observe the atom's line of motion. The velocity of an atom can be deduced from the temperature of the vapor from which it has emerged by means of the kinetic theory of gases. As a matter of fact it may be measured experimentally according to the ingenious method devised by Stern (see Chap. III). If the atom has no magnetic moment, s (in the formula) becomes equal to 0 ($s = 0$), since the diamagnetic influence—which every atom, even a paramagnetic atom, experiences to a greater or less degree—is vanishingly small.

We will outline briefly the method of procedure adopted in these experiments. S in Figure 27 represents a sharp edge several centimeters in length of a wedge-shaped pole-piece of a strong electromagnet. M is the opposite pole-piece. An atomic ray emerges from the vapor space D (e.g., a small heated chamber filled with silver vapor) and after passage through two slits B is sent parallel and close to the sharp edge of the wedge-shaped pole-piece into an inhomogeneous magnetic field. At the end of the field a plate *P*, upon which the atomic ray will impinge, is set

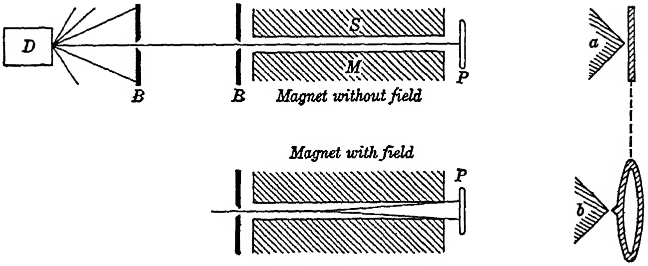


FIG. 27. Schematic arrangement of atomic ray experiments.

perpendicular to the direction of the beam. The relative position of *P* with respect to the pole, compared with the distance of the latter to the slit *B*, makes possible the calculation of the path traversed by the atomic ray while in the magnetic field. In this way Gerlach and Stern investigated the deportment of silver rays. When the plate *P* was developed into visibility by methods outlined in Chapter III, it was found that the atomic rays had condensed along two lines. This indicated a deflection of the ray and its separation into two discrete beams which were deflected in opposite directions. Figure 28 reproduces an enlarged photograph showing the trace left upon the plate *P* when no field is applied (*a*) and with an applied field (*b*). To comprehend this more fully there is added in Figure 27 a diagrammatic sketch of the atomic ray and its traces upon the plate *P*. The line in (*a*) represents the trace of the ray upon the plate when the field is absent, (*b*) shows how the magnetic field has split the atomic ray into two discrete sections, the splitting being the more pronounced the greater the field of inhomogeneity, i.e., it is greatest in the line of symmetry of the field. From the extent of this observed deflection—it amounted to 0.1–.25 mm.—and from the known velocity of the rays and the measured inhomogeneity we may deduce the magnitude of the magneton to be 5,550 absolute units per mole. If

Avogadro's number be taken as 6.06×10^{23}, this will give a value of 9.2×10^{-21} as the moment for the individual atoms, a value which is identical with the calculated magnitude of the Bohr magneton.

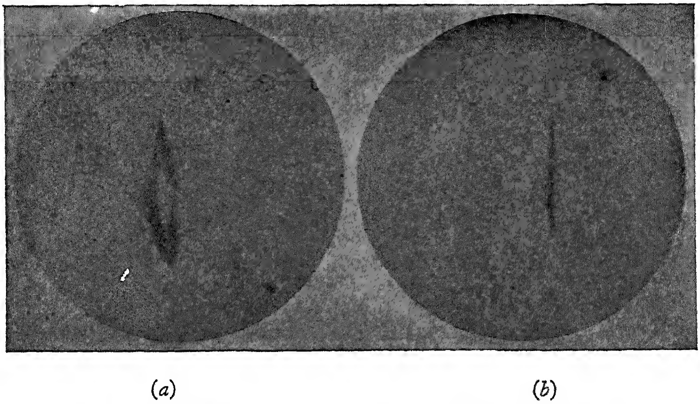
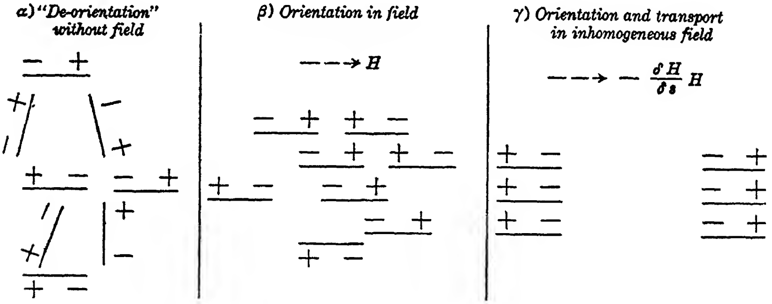


FIG. 28. (*a*) Without magnetic field; (*b*) with magnetic field.

We may now speculate as to the reason of this splitting into two discrete beams while in the magnetic field. How explain this effect? The splitting of the ray becomes readily intelligible if it is assumed that the magnetic axes of all atoms coincide with the direction of the field, the atoms being so orientated that the sign of the moment of half of them coincides with that of the field while the sign of the remainder is opposite to that of the field. We shall term these two positions respectively the parallel and the anti-parallel positions of the atoms. On these assumptions the influence of a magnetic field upon the atomic ray may be represented as in the following diagram.

The phenomenon of the splitting of the atomic ray is of great import to our theoretical knowledge. Sommerfeld has designated this orientation of the atoms as "directional quantization."

On the quantum theory the moment of momentum is equal to $\pm h/2\pi$. Accordingly, the atom must so place itself that the plane of the orbit in which the electron is revolving (i.e., its molecular stream) must be perpendicular to the direction of the magnetic force. This, however, does not specify the sense of rotation of the electron, i.e., the electron may rotate in the plane of its orbit either right-handedly or it may rotate left-handedly. Such a condition obtains when the moment axis is either parallel or anti-parallel to the field. In the absence of a magnetic field, as in (*a*), the atomic axes assume haphazard positions; in a magnetic field, however, two directions are possible, viz.: the parallel (*b*), as is shown schematically in the following diagram, which depicts the orientation of the atomic moments in the absence and in the presence of a magnetic field. In other words, it indicates the readjustment of the atomic axes taking place as the ray enters into the confines of the magnetic field.



In the diagram, α, β, and γ indicate the several genetic steps involved in the experiment described above. A. Sommerfeld's designation of this mode of atomic readjustment in a magnetic field as "directional quantization" is in great use. It will not be amiss at this point briefly to comment upon the essential differences in the behavior of the atoms as postulated by the quantum theory on the one hand and their anticipated behavior from the viewpoint of the classic theory on the other. Suppose atoms possessing magnetic moments to occupy random positions in a "field-free" space as in (*a*); on the application of a magnetic force these atoms will execute, on the classical theory, a uniform rotation about the field direction without changing the angle made by the moment axes with the field direction (Larmor's precession movement). That is, all directions of the atomic moment are equally likely. An atomic ray composed of such precessing atoms would merely be broadened in an inhomogeneous field and not resolved into two discrete rays. Experiment, therefore, decides unequivocally in favor of the quantum theory of magnetism inasmuch as it

(1) demonstrates directly directional quantization;
(2) quantitatively yields Bohr's magneton.

Experiment demonstrates that an atom having a magnetic moment of one Bohr magneton can assume but two positions in an exterior magnetic field. These two positions are distinguished by a small difference in their energy contents since energy is consumed in the rearrangement of an atom from any one position into the anti-parallel whereas an equivalent amount of energy is liberated when an atom reverts to the parallel position. Hence, such an orientation can be maintained only if there are no other additional forces operative upon the atom; for in that case the "anti-parallel atoms" would suffer a derangement and be transposed into the position of lower energy, i.e., into the more probable parallel position. Such a derangement, however, does not take place in the atomic ray experiment because the succession of atoms in the ray is so infrequent that the moving atoms do not mutually collide. Moreover, no direct indication of such derangement has been noted to date, even under conditions where a marked positional readjustment may be anticipated, e.g., in paramagnetic gases and solutions whose magnetic constants are highly suggestive of a directional quantization. We must conclude accordingly that this unknown (and, for that matter, unintelligible) orientation mechanism operates so rapidly that the thermal impacts in compact matter do not influence the time consumed in the orientation of atoms, ions, or molecules. All these problems still present serious theoretical difficulties. It is significant to remark in this connection that the twofold orientation of the atoms is the outcome of an experiment free from hypothesis and from theory, and which today is best explained by the theory of directional quantization.

Sommerfeld extended the theory of quantization to atoms having more than one moment quantum, that is, to atoms with several magnetons. Thus, atoms with *J*-magnetons so orientate themselves in a field that the component of the moment coinciding with the field is expressible as a whole numbered multiple of the unit $h/2$. Atoms with *J*-moments can therefore set themselves only in such directions that their axes will be inclined to the field direction by $\cos \phi = j'/j$ ($j' = 1, 2, 3, \cdots j$). An experimental example illustrative of such an adjustment is not yet available. Figure 29 represents an atom with $J = 3$. This may be explained as follows: some of the atoms will set themselves with axes $\pm 3M$ in the direction of the field (as the silver atom with $1M$). A second portion will precess at the angle $\cos \phi = 2/3$, and still another portion of the atoms, at the angle $\cos \phi = 1/3$, about the direction of the field, so that the component coinciding with the direction of the field will be $\pm 2M$ or $\pm M$, respectively.

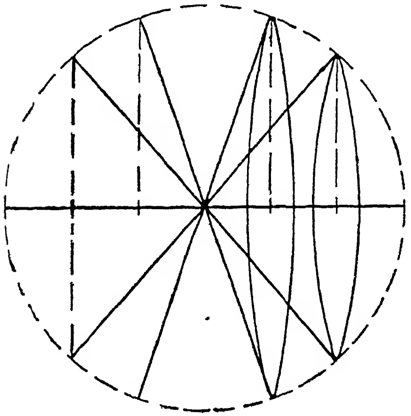


Fig. 29.

To date, the magnetic behavior of the greater number of atoms has been investigated. All the atoms of the first vertical column of the periodic system, i.e., the univalent alkalis and the noble metals, have a magnetic moment of one Bohr magneton. The elements of the second vertical column, the alkali earths, have no moment. These elements are characterized by an even number of electrons, whose individual moments obviously neutralize one another just as the moments of all the electrons of the alkalis do, excepting that of the one valence electron. In like manner the elements of the fourth column and the noble gases of Group *O* do not exhibit magnetic characteristics. All these elements likewise have an even number of electrons.

There is still another theory as to the atomicity of magnetism, which is purely empirical, viz.: the method of P. Weiss according to which the magnetic constants of matter are reducible to a definite unit, which, as an elementary magnet, is a constituent of all magnetic matter. This unit is the so-called "Weiss magneton." The magnitude of this unit is so determined that the magnetic moments of all paramagnetic substances, calculated per mole, are expressible as whole multiples of it and it is equivalent to 1,123 absolute units. Numerically this Weiss magneton does not agree with the Bohr magneton. However, its magnitude is within 1 per cent the fifth part of Bohr's unit. The physical significance of this fact is not known to us. On the other hand, it has been shown time and again (Pauli, Epstein, Gerlach, Sommerfeld) that Weiss' magneton numbers may be reduced with the aid of plausible assumptions to Bohr's unit. There is no doubt, however, that the experimental results of Weiss, Cabrera, and their coworkers are not all explainable in the sense of the quantum theory. Nevertheless we may anticipate confidently that the intensive experimental inquiry to which this problem has been subjected recently will soon unravel and clarify some of these perplexities and bring light into darkness.

Another problem may be treated in this connection, viz.: the problem whether other physical phenomena are modified by such an atomic adjustment. Optical phenomena immediately come to the mind. Let us assume an atomic gas in a magnetic field, and that all the atoms possess a magnetic moment of one Bohr unit. According to the explanation of atomic ray experiments, all the electronic orbits would set themselves perpendicular to the lines of force. If a light beam be transmitted through a magnetic gas perpendicular to the lines of force so that the electric vector of the light vibrates sometimes parallel to the electron orbits and at other times perpendicular to their plane, a different propagation velocity may be expected for these two rays. In other words, we may anticipate a magnetic double refraction whose magnitude must be independent of the magnitude of the field, of the wave-length, and of any special atomic type, provided only that they are magnetically equivalent. Within recent years many comprehensive investigations have been undertaken to establish the existence of such an anticipated effect. Yet, even the most sensitive apparatus has not succeeded in detecting the slightest indication of such double refraction. Especial interest attaches in this connection to the recent thorough researches of W. Schütz.[2]

Experiments on the influences affecting the reaction velocity of the chemical reaction between the paramagnetic gases, oxygen and nitric oxide, have been carried out by A. Kornfeld. It was found the reaction was accelerated by the magnetic field. We have here a most interesting fact, although explanation of it will be premature until more exhaustive measurements are available.

Finally, brief reference will be made, in passing, to the researches of A. Glaser on the diamagnetism of gases which were explained for some time as a directional quantization effect. Glaser observed that the susceptibility of a gas increased anomalously with decreasing densities. The explanation offered for this was somewhat as follows: due to the fewer numbers of gas kinetic impacts in gases under diminished pressure (i.e., lower densities), the orientation of the atoms should be apparent in their magnetic behavior, while the increasingly larger number of impacts at higher pressures destroys the atomic readjustment. E. Lehrer[3] attempted to corroborate this data with other methods but he failed completely to obtain even an indication of the effect noted by Glaser. We are inclined therefore to hold to the view that the specific susceptibility (i.e., the mass susceptibility) of a gas is independent of its density.

[2] See articles in Zeitschrift für Physik, 1926.

[3] Tübingen Dissertation, 1926.

We may state in general, therefore, that we have, to date, no evidence of atomic orientation apart from the experiment on directional quantization. This directional quantization experiment is of especial significance in that it yields experimental evidences of the existence of definite atomic conditions. Thus, the Zeeman-Effect, the splitting of spectral lines under the influence of a magnetic field, has been explained by Debye and by Sommerfeld on the basis of directional quantization. We will not, however, enter into a discussion of this problem at this point.

CHAPTER IX

SUPER-CONDUCTIVITY[1]

For quite a while the phenomena of electrical conduction by metals were explained satisfactorily on the basis of the electron as the elemental quantity of electricity. By this theory (proposed by Drude) there are present in a metallic conductor, in addition to its atoms (ions), "free" electrons whose mean kinetic energy ($= \frac{1}{2}\mu v^2$) is assumed equal to that of the atoms ($= \frac{1}{2}MV^2$). The velocity (v) of the electrons, proportionate to their smaller mass, is $\mu\sqrt{M/\mu}$ times greater than the velocity of the atoms. (Due to the close packing of atoms in a metal it is highly probable that the electronic orbits of two or more atoms overlap. Obviously, therefore, planetary electrons may penetrate within the sphere of influence of two adjacent atoms, whereby they may tend to satisfy simultaneously the demands of the two atoms. Under such conditions, some electrons may be dislodged from their respective orbits about their atomic nuclei, there being imparted to them a freedom of motion more or less random in character, collisions occurring between electrons or between electrons and atoms in a manner analogous to the collisions of gaseous particles.) Under the influence of an electric field—potential difference maintained between the two ends of a metallic strip—there will be superimposed upon the "Brownian movement of the electrons" a directed motion along the lines of force of the field. Proceeding from such assumptions, the electrical conductivity (reciprocal specific resistance) of metals is given by the expression,

$$\sigma = \frac{\epsilon^2}{2\mu v} N\lambda,$$

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[1] The older literature has been compiled by W. Cromelin, Physikal. Zeitschr. 21, 274, 300, 331 (1920); more recent work is listed in the Rep. and Communication of the 4th Intern. Congress of Refrig. London, 1924. Further, see also Festschrift zum 40 jahr. Professorat von Kammerlingh-Onnes, Leyden, Eduard Ydo, 1922, Vol. 5.

in which ϵ, μ, v and λ designate respectively the electronic charge, mass, velocity and free path, i.e., the path traversed by an electron between two successive collisions, and N the number of electrons per unit volume. Taking $\frac{1}{2}\mu v^2 = \alpha T$ (absolute temperature), the above equation becomes

$$\sigma = \frac{\epsilon^2 \cdot v \cdot N \cdot \lambda}{4\alpha T}.$$

The latter form[2] expresses the relation of conductivity to absolute temperature. According to the classical kinetic theory v decreases progressively as the temperature is lowered, becoming infinitesimally small at temperatures in the neighborhood of absolute zero. Such a variation in v, of necessity, operates to produce a proportionate decrease in σ. In other words, at very low temperatures, the electrical conductance of metals should vanish completely. The correctness of this theoretical inference may be tested by direct experimentation since the successful liquefaction of helium by Kammerlingh-Onnes has placed at our disposal this efficient means for low temperature production. In the following table are presented attainable low temperatures, expressed in absolute units, together with the substances whose liquefaction from the gas state takes place, under the proper pressure, at the corresponding temperatures.

Boiling Points of the Condensed Gases at Normal Pressure

Liquid Oxygen	91.0° Abs.
Liquid Nitrogen	77.3° "
Liquid Hydrogen	20.4° "
Liquid Helium	4.3° "

Still lower temperatures may be obtained if the pressure above the boiling liquid is lowered; it is especially possible by this means to obtain constant intermediate temperatures by the proper operation of the pumps.

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[2] (On the assumption of the classical kinetic theory $\frac{1}{2}\mu v^2 = \frac{3}{2}KT$ or $= \frac{3}{2}K$. The equation thus becomes $\sigma = \frac{\epsilon^2 \cdot v \cdot N \cdot \lambda}{6KT}$, where K is the Boltzmann constant.) Tr.

The following table lists a few substances and their corresponding temperatures and pressures.

Substance	Pressure	Temperature (Abs.)
Nitrogen	100 mm.	63.6° (at 760–77.3)
Hydrogen	50 “	14.1° (at 760–20.4)
Helium	760 “	4.3°
“	3 “	1.5°
“	0.1 “	1.0°
“	0.05 “	0.89–0.94°
“	0.01 “	0.79–0.825°
“	0.005 “	0.74–0.785°
“	0.001 “	0.65–0.71°

Our knowledge of the conductance of metals at very low temperatures is due almost entirely to the remarkable work of Kammerlingh-Onnes and his coworkers. In his laboratory at Leyden the resistance coefficients of many metals were measured at extremely low temperatures. The observations made by these investigators proved very astonishing since their experimental data not only did not conform to the theoretical expectations described above, but indicated a phenomenon exactly opposite to that predicted by theory. Instead of observing the anticipated gradual increase in the resistance with progressively decreasing temperature, there was noted, for certain metals, a very sudden and more rapid falling off in resistance than is accounted for by theory. In some instances, this decrease proved so extensive that it was impossible to measure the resistance of the material, i.e., a measurable potential difference could no longer be maintained at the ends of the current-bearing conductor; nor was an increase in temperature of the conductor detectable. The resistance had practically vanished. Metals characterized by such an anomalous behavior are said to be in the “super-conductive” state.

The following metals became super-conductive: mercury, lead, tin, indium, thallium, and their alloys. In all cases the transition from the normally conducting to the superconducting state was instantaneous and sudden. The “transition” temperatures measured for these substances are recorded in the following table.

Lead	7.2°	Abs.	
Radiolead	7.2°	"	
Lead-tin alloy	7.2°	"	(about)
Tin-amalgam	4.29°	"	
Mercury	4.15°	"	
Tin	3.78°	"	
Indium	3.41°	"	
Thallium	2.32°	"	

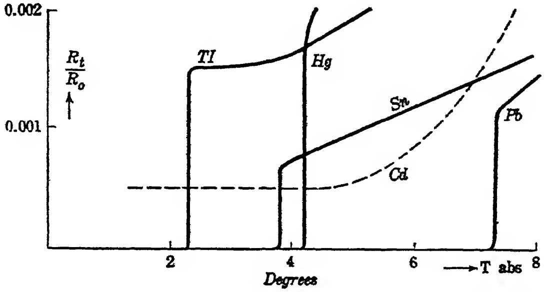

FIG. 30.

Figure 30 illustrates the suddenness with which this phenomenon makes its appearance. In it the ratio of the resistance at the experimental temperature Absolute to that at 0° C. is plotted along the ordinate axis as a function of the experimental temperature as abscissæ. This ratio becomes equal to zero, when $R = 0$. The actual magnitude of the resistance below the "transition" temperature is determinable only by assigning to it an upper limit; at all events it is 10^{12} times smaller than the resistance at 0° C. and independent of the current strength acting upon the metal. Only when this current strength is of a definite "threshold value" which depends upon the temperature at which the metal is held, does a very sudden heating effect, i.e., increase in resistance, take place. In the experiment with mercury a current density of more than 1,200 ampere/mm.^{2} was found necessary and for lead 560 ampere/mm.^{2}. It is noteworthy, however, that Ohm's law is valid in all cases and holds right up to the "transition" temperatures. The dotted curve gives the data of R_T/R_0 for a non-supraconductive metal, cadmium (see below).

Alloys of supraconductive metals appear to become supraconductive at that temperature at which the component with the highest "transition" temperature becomes supraconductive. Especially remarkable in this connection is the fact that gold and cadmium amalgams become supraconductive at about 4.15° A., although neither gold nor cadmium, but only mercury, exhibits the phenomenon of supraconductivity. Non-supraconductive metals coated with a thin film of supraconductive material likewise become supraconductive. However, such thin films seem to become supraconductive only at lower temperatures than the massive and unalloyed material.

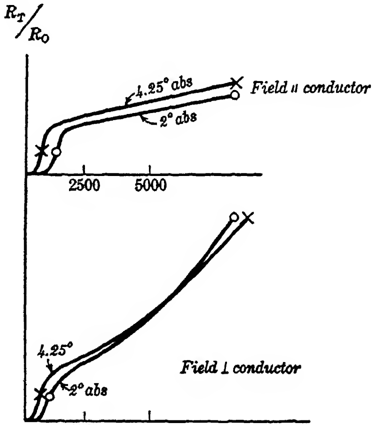

Fig. 31.

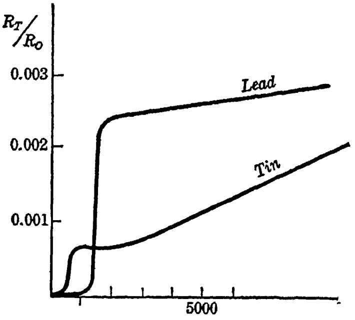

Fig. 32.

Furthermore, this phenomenon of supraconductivity is suspended by a magnetic field. Here again there is evidence of a "threshold value" which occurs at higher fields, the lower the temperature at which the supraconducting metal has been held. This relationship may be depicted graphically (Fig. 31) by plotting the ratio of resistances R_T/R_0 as a function of the magnetic field for two different temperatures. A marked similarity between these curves and those in which the resistance is plotted as function of temperature (Fig. 30) is readily perceivable.

This effect is in harmony with the well-known extraordinarily large increase in the Hall-Effect and in resistance brought about by an exterior magnetic field with decreasing temperature.

Figure 32 depicts comparative measurements made upon two supraconductors regarding the establishment of normal conduction in a magnetic field. Here again is evident a similarity to the corresponding temperature-transition curves.

We may attempt so to relate the cessation of supraconductivity occasioned by a magnetic field of definite intensity to that resulting from a fixed current density, by attributing the later effect to the magnetic field generated by the current. Indeed, calculations show that, for the critical density which is requisite for the cessation of supraconduction, the field generated about the surface of the wire has an intensity of 500 gauss.

It is interesting to note that the supraconductive metals have a lower transition temperature when subjected to mechanical tension. X-ray examinations of the structure of the metal (crystalline form) in the supraconductive condition were performed by Keesom, and no changes of any kind could be noted.

Not all metals become supraconductive. Nevertheless, these, too, exhibit an anomalous behavior, more or less contradictory to the theoretical considerations outlined above. Instead of exhibiting an increased resistance with lowering temperature, their resistance falls to a minimum, retaining a constant value with a further drop in temperature, that is, a gradual disappearance of the coefficient of resistance. Metals of this class are gold, platinum, cadmium, aluminium, sodium, potassium and iron, whereas gold amalgam and cadmium amalgam, as already stated above, exhibit the property of superconductance. The data obtained from measurements upon very pure platinum wire (0.1 mm.) are reproduced in the following table and in Figure 33 respectively.

$T_{abs.}$	R_T/R_0
273°	1.0000
20.2	0.0171
14.2	0.0135
4.3	0.0119
2.3	0.0119
1.5	0.0119

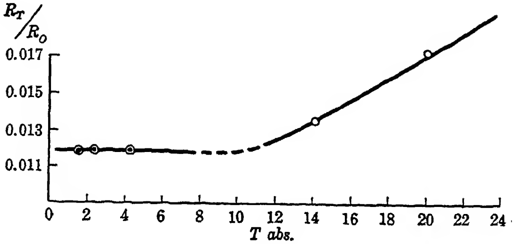

FIG. 33.

Sodium and potassium, subjected to several distillations and solidified in glass capillaries (treated exactly as mercury)., gave the following values for R_T/R_0 between 4.2 and 1.5 Abs.

Sodium, 1 Test—$R_T/R_0 = 0.0038$,
Sodium, 2 Test—$R_T/R_0 = 0.0047$,
Potassium —$R_T/R_0 = 0.0099$.

In this regard, we must also reckon with the possibility that this interval of constant resistance (Rest-Widerstand) may be ascribed to the presence of impurities, since the ratio R_T/R_0 becomes smaller, the purer the metal. The divergence in the values of the two sodium tests is also noteworthy.

There is still a third class of metals which retain their normal (positive) coefficient of resistance even at very low temperature. By a peculiar coincidence this behavior is typical of those alloys which do not exhibit a normal coefficient at higher temperatures. Among them we find manganin, whose resistance, as is well known, varies but slightly with temperature.

So much for the experimental data, the correctness of which is highly obvious. It is not feasible at this time to speculate too deeply regarding these peculiar anomalies or to seek theoretical explanations for their occurrence, although several such explanations have been proposed. At best, however, these are not sufficiently definite and precise. It seems wise, accordingly, and more consonant with the facts to delay serious consideration of these "explanations" so as to avoid a needless pro and contra discussion of their relative merits. There may be operative at these low temperatures some unknown influence explainable perhaps by the quantum theory: "free electrons" as ordinarily interpreted are absent in metals. Furthermore, we know now that the conductivity of a material is not a specific constant, but depends upon its inner structure; not only is the conductivity of thin films different from that of denser films, but different likewise along the crystal axes. Indeed, the vanishing of the temperature coefficient of conduction (which is approximately equally large for all pure metals and whose value is near that of the thermal expansion coefficient of gases) of thin films itself may be regarded as a type of supraconduction.

Attention may be directed finally to a series of experiments, the results of which, although extremely self-evident and intelligible, proved nevertheless very astonishing. We refer to the experimental demonstration of the persistence of an electric current in a metal while in the superconducting state. An induction current is generated in a supraconducting coil by reducing to zero the intensity of a magnetic field cutting the plane of the coil. The current so produced meets with an extremely small resistance and accordingly will spend itself slowly whereas the normal period of relaxation is of an exceedingly brief duration. The presence of a current in the superconducting coil may be demonstrated by the behavior of a magnetic needle placed in the neighborhood. As a matter of record one such current continued fairly constant, its intensity falling off less than 1 part in 20,000 in the interval of one hour.

This method was further elaborated within recent times. By its means a result, already mentioned above, was confirmed, viz.: that the electrical resistance of a substance in the supraconductive state is less than $1/10^{12}$ of its value at 0° C.

We are still in the dark in regard to the question as to whether pieces of two supraconducting metals riveted one to another retain their supraconducting property. Recent communication on this subject shows that 24 tin and lead wires soldered to one another no longer were superconductive. This is at variance with previously published results. Confirmation of these data will indicate a relation with crystal structure.

CHAPTER X

Crystal Conduction

The phenomena which attend electrical condution in solid, liquid, and gaseous matter differentiate two types of conduction, designated respectively as electronic conduction and ionic conduction. The former embraces all those conductions in which the electricity moves through the conducting material without producing in it a detectable irreversible change. For ionic conduction, on the other hand, the quantity of electricity transported is associated so intimately with material constituents that both migrate jointly; so much so that a transport of electricity is impossible without an accompanying transport of matter.

Consideration of the state of aggregation of the conducting material in no way helps to determine in which way the substance will conduct. There are solid bodies that conduct electronically and others that conduct ionically; both ionic and electronic conduction take place in gases; and finally, there are liquids that conduct electronically and others again that are conductive ionically. The electronic conduction of a certain class of solids, viz.: the metals, is treated separately because of its significance, the term "metallic conduction" being applied to it. Liquid metals, metallic alloys and metalloids also act similarly. Electronic conduction in gases presents a special case: the convection of free electrons without collisions with gaseous atoms (cathode rays).

Electrically conducting liquids—apart from liquid metals and alloys—conduct ionically, as do fused salts and solutions of acids, salts and bases and gases at high pressures.

We will now enumerate the typical phenomena which characterize ionic and electronic conductions respectively. The most characteristic mark of ionic conduction consists in the transport of matter. Ions, i.e., equal numbers of positively and negatively charged molecules or atoms, are present in an ionically conducting liquid. When this is subjected to an electric field, i.e., if a fall in potential is applied, the ions migrate, under the influence of this electric force, with a specific mobility to the oppositely charged electrode where they loose their charge and are disengaged as neutral atoms, molecules or radicals; or they may be altered, subsequent to their discharge, because of some chemical interaction taking place at the electrode, the chemical action being independent entirely from the electrical phenomenon. Pure ionic conduction takes place in salt solutions, fused salts, and in the so-called "electrolytes." The quantitative phenomena of electrolysis and the transport of matter are expressed in Faraday's law, while Ohm's law is applicable to the current. The validity of this law for extreme cases has been substantiated recently by the very exact work of M. Wien.

As opposed to this electrolytic conduction, metallic conduction does not involve a transport of matter. Our views regarding metallic conduction are based entirely upon the fundamental assumption that electrons are present in the metal which may be considered as "free" with respect to the smallest electric charges. Since the metal, taken as a whole, is electrically neutral, we must assume an equal number of metal ions and of "free" electrons. We might anticipate, on a priori grounds, that, under the influence of an electric field, equal numbers of electrons and of ions should move through the metal. No such motion has been observed, to date, for the latter; in other words, metallic conduction takes place without change in matter—unless such a change may be attributed to the heat of the current—without any displacement of matter. Ohm's law is valid for any high or low current densities. This validity has been confirmed anew in recent times by Rausch v. Traubenberg, who loaded wires of 0.05–0.1 mm. diameter with 10^5 amperes per square millimeter without ascertaining a notable departure from Ohm's law.

Metallic conduction is characterized in general, therefore, by the validity of Ohm's law and the absence of a transport of matter. We are still confronted, however, by the question whether it is at all possible to demonstrate directly the migration of the electrons. An attempt to show that electrons have motion by means of inertia effects, that is, by passing the current through very sharply curved conductors so that the electrons by virtue of their inertia would continue on rectilinearly, proved unsuccessful. The direction of the magnetic field surrounding a current-bearing wire suggests a motion of negative charges within the metal. Free electrons —cathode rays—may be curved along circular paths by means of exterior magnetic fields; metallic conductors were investigated accordingly along similar lines in the course of which certain phenomena were noted which indicate a similar effect; the phenomena are so complicated, however, that they do not lend themselves to easy discussion. We must remark, nevertheless, that part of this complex effect (called Hall-Effect) has been attributed to the microcrystalline structure of the metal in use.

Solid ionic and electronic conductors may be differentiated in still another way. We may designate also as ionic conductors such crystals which insulate electrically but which are built up of ions (more about these later). Their insulation is due—according to these views—to the fact that the internal binding forces operative between the oppositely charged ions are greater than the electrical separation forces attainable by means of exterior fields. The difference between the two groups of conductors lies in their optical behavior, in their reactions toward incident light. Metals are marked by their high reflection and absorption power, due, no doubt, to the great reactivity of the "free" electrons upon electrical forces, in the present instance upon the electric field of the light. Ionic conductors, in the above sense, on the other hand, are permeable, i.e., transparent, to electro-magnetic vibrations. But this transparency obtains only for a fixed range in frequency in somewhat the same manner that optical reflection from metals is dependent upon the frequency. As is known, this latter problem constitutes an essential part of Maxwell's electromagnetic theory of light. We will not discuss, however, at this point those considerations which deal, for example, with the increase of reflection from metals with increase in wave-length and which express in conformity with experimental results the connection between the conductivity constant and reflection. We will consider, rather, a few problems intelligible from an atomistic point of view. Crystals exhibit, just as do the metals, the phenomenon of metallic reflection for certain definite frequencies, viz.: the "slow" frequencies (infra-red radiation) of the incident radiation which correspond to the specific vibration frequencies of the ions in the crystal grating. We shall enter into a more thorough treatment of this phase in subsequent chapters. In addition, crystals also are opaque to certain "rapid" vibrations (short waves) of the incident light; these vibrations correspond to specific frequencies of the electrons in the ions of the crystals that are understandable theoretically but not yet interpretable from an atomistic viewpoint. To visualize more clearly the possibility of such frequencies, let us consider the characteristics of a monatomic gas. A monatomic gas is transparent for most all wave-lengths; and yet, light is propagated more slowly in such a gas than in a vacuum, the propagation velocity being different, indeed, for each wave-length. This suggests, unmistakably, a mutual interaction between the radiation frequency and the electrons present in the individual atoms. An atomistic interpretation, either model or formal, of this dispersion phenomenon is completely lacking today. However, certain very sharply defined frequencies are absorbed by a monatomic gas, to wit, those frequencies which the atom is capable of emitting upon appropriate stimulation. The quantum explanation of this phenomenon is treated in Chapter XVII. As a second example let us take a molecular gas, as water vapor or carbon dioxide. They, too, are transparent up to certain long-waved frequencies which correspond to the resonance of the inner vibrations of the atomic constituents of the molecule, e.g., H-O-H, C-O-O; they are transparent likewise to definite frequencies in the short-wave spectral region which are to be interpreted in a manner similar to the absorption frequencies of monatomic gases. Finally, all matter, even the metals, is transparent, in turn, to very short wave-lengths (X-rays, γ-rays) up to certain specific and characteristic frequencies for each atom which are in resonance with the vibrations of the inner atomic electrons.

Very comprehensive experiments on the conductivity in solid crystals and on the question of the validity of Faraday's law have been performed by Haber and Tollutzko and later by Tubandt (partly in conjunction with R. Lorenz). For most of the crystals investigated, it was established that they show pure electrolytic conductivity, i.e., they are ionic conductors. Tubandt satisfactorily explained why a large number of previous measurements had led to uncertain results. He observed that cathodic deposition of metals during electrolysis of crystals takes place in a manner analogous to the separation of zinc and lead in the electrolysis of salt solutions, i.e., in the form of "dendrites," ramified threads of closely cohering metal which grow inward into the electrolyte, in this instance, into the crystal. In addition, Tubandt noted that certain crystals exhibit not only electrolytic conduction, i.e., ionic conduction, but electronic conduction as well. β-Ag_2S is such a crystal. It is extremely probable also that oxides are mixed conductors as is evident, for example, in the complete change in the optical behavior of silicon dioxide at high temperatures, which is highly suggestive of a change in the nature of conductivity, i.e., a transition from ionic to electronic conduction. It may be remarked, furthermore, that Tubandt has demonstrated that conduction is attended in many crystals by the migration of only one ion. The reason for this is not obvious at present. It is very likely, however, that this phenomenon is not so much a characteristic of ionic conductance in crystals but rather the effect of extreme differences in the respective mobilities of two ions. Obviously, many unsolved problems still confront us.

During recent years the systematic experiments of Gudden and Pohl[1] have made available many interesting results that have contributed decisively to the solution of the problem of photo-conductivity in crystals. They examined particularly the diamond and crystals of zinc sulphide. In the dark and at room temperature these crystals are remarkable insulators, even for rather high potentials. Slightest exposure to light, however, renders them conductive. The first investigations of this light effect yielded rather complicated results. Eventually, they succeeded completely in explaining the cause of these complexities and in recognizing and distinguishing two essential effective factors. Photo-conductivity is initiated by a photo-electric effect, i.e., it is due to the release of electrons in the interior of the crystal by means of absorbed light energy. These released electrons migrate under the influence of the applied potential difference and constitute the primary current. Their displacement obviously disturbs the crystal grating as a result of which an increase in conduction sets in. Gudden and Pohl designate this current increase as "secondary current." The primary current exhibits extraordinarily simple relations. It begins immediately at the first moment of illumination. It is proportional to the intensity of the absorbed light, and the extent to which the current stream is illumined. Furthermore, it becomes saturated at a definite potential. Quantitatively, the saturation stream is expressed by the number of light quanta absorbed per second so long as the effective light does not lie in the region of the selective crystal absorption. (In this last mentioned region the saturation current amounts to only a small fraction of the theoretical amount.) The secondary current doubtless is electrolytic in character, although the available data concerning its nature are so exceedingly complicated that we will refrain from discussing them at this time.

An important result in connection with the photo-electric

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[1] Numerous contributions in Zeitschr. f. Phys. 1921–1926.

conductivity of crystals was noted by W. Lenz. He observed that the photo-electric primary current exhibited the normal Hall-Effect but that its magnitude and indeed its very origin are dependent upon the orientation of the crystallographic axes with respect to the electric and magnetic fields respectively. If the experimental conditions are so chosen that the Hall-Effect makes its appearance, it will indicate, even more clearly than ever observed for metals, the correct sign of the electronic deflection and its reversal with the change in field direction.

We may affirm, therefore, that the conductivity phenomena in crystals which at first seemed so severely complicated—to which the much discussed selenium problem belongs—are today more thoroughly explained theoretically and experimentally than the electronic conduction in metals. Furthermore, we may cherish the hope that the eventual explanation of metallic conduction is contained potentially in the experimental results of Gudden and Pohl.

CHAPTER XI

(*a*) TRANSFORMATION IN THE PHYSICAL CONDITION OF ATOMS

(*b*) QUANTA-EXCITATION OF LINE SPECTRA[1]

Of more immediate importance than the existence or non-existence of atoms, their permanence and their relative stability, is the problem of the possible transitory transformations that may take place within the atoms. The spectral emissions of the chemical elements, as variously observed in their respective line spectra, in the bunsen flame, the luminous arc, in Geissler tubes and in the spark, consist in a release of energy, in the form of radiation, from the "glowing" atom. It has been established, fairly definitely, that the energy so released emanates directly from the atom itself and is not a concomitant or consequence of chemical reactions. Of course, the excitation energy can originate from the heat of a chemical reaction. We will discuss this in a subsequent chapter (XXV). Obviously, the atom must absorb energy prior to the emission by it of its characteristic spectrum. It may now be queried: which of the atomic constituents is the effective factor primarily operative during the period of radiation? The answer: one of the orbital electrons present within the atom induces radiation, which may perhaps best be shown from a study of the Zeeman-Effect, i.e., the influence of a magnetic field upon the emission. Furthermore, it has been observed qualitatively that a given atom may be stimulated to emit various spectra according to the intensity of the energy imparted to it. Throughout the following discussions, therefore, we shall assume that the absorption of energy (the atomic excitation) and its consequent disengagement (spectral emissions) are consummated within the electronic structure of the atom.

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[1] These theoretical problems are discussed by A. Landé, Forschungsberichte 4 (1921). The experimental bases are treated in thorough manner by W. Gerlach in "Experimental Bases of the Quantum Theory" (published by Vieweg & Son, 1921).

Generally (except in the case of electro-negative atoms) (see Chap. XXVI), energy is required to effect variations in the electronic structure of a normal atom, either as regards the number of the electrons or their spatial configuration. The change, so induced, in the physical condition of the atom is of temporary duration only and devoid of all permanence. Secondary effects, arising during the course of such a transformation, will receive separate and ample treatment in subsequent chapters (see photochemistry, etc.). Furthermore, an atom need not, of necessity, absorb every energy imparted to it. Atomic alterations are conditioned, therefore, upon definite factors characteristic of the particular energy absorbable by the atom. This is one of the basic conclusions which Bohr draws from the fact that each element emits a limited number of spectral lines, i.e., discrete spectral lines peculiar to each element. Except in cases of metastability which will receive special discussion later, the reconversion of the altered atom into its original normal condition takes place spontaneously without simultaneous actuation by exterior influences, provided the change involved primarily the position or localization of one or more electrons. On the other hand, if the transformation resulted in a variation in the number of electrons, e.g., a decrease, a return to the normal atomic structure may ensue only if the proper opportunity is offered the altered form to recombine with the necessary number of electrons.

Three methods are available whereby energy may be imparted to atoms: kinetic energy arising from atomic impact (heat energy), energy produced by electronic impact, and, finally, energy in the form of radiation (absorption).

For simplicity of discussion, let us assume the atoms are individually and mutually independent of, and without influence upon, one another. Apparently, this condition tends to prevail if the atoms are present in a highly rarefied, monatomic gaseous state. Addition of heat to atoms, so constituted, increases their kinetic energy. When two such atoms collide, an impulse proportionate to their relative velocities (and consequently to their respective kinetic energies and temperatures) will be conveyed from one impacting atom to the other. Such an energy transfer, however, does not necessitate a change in the structure of the recipient atom, which is foreign to the mechanism of such a process from the viewpoint of the kinetic theory. On the other hand, it may be assumed, feasibly, that heat energy can induce a change within an atom if it absorbs the kinetic energy of the impact, storing it in some manner as potential energy and eventually utilizing it to accomplish a change in its own physical condition. As a matter of fact, such changes are known to us, e.g., the dissociation of diatomic gases at elevated temperatures. As stated above, such variations in atomic structure cannot be induced by the absorption of energy selected at random. A definite energy is required for each change. If we know the energy E necessary to convert a specified atom into some other condition (which energy is likewise absorbable by the atom), we can determine the per cent of unaltered atoms that are in thermal equilibrium, at a definite temperature and pressure, with the corresponding altered forms. This may be accomplished according to accepted physical-chemical principles applied to the reversible reaction,

$$\text{Atom} \rightleftarrows \text{Changed atom}_1 - E_1,$$
$$\text{Atom} \rightleftarrows \text{Changed atom}_2 - E_2.$$

Furthermore, Boltzmann's equation P prop. $e^{-E/KT}$ enables us to state the probability P with which a particular atomic condition obtainable by the absorption of energy E will be present for a given temperature. The quantitative explanation of the temperature-luminosity of gases is based upon this. We shall apply similar considerations to a special problem in Chapter XXX.

The relations expressing the addition of energy to atoms as a result of impact by electrons in motion are of a more distinct nature and more accessible to quantitative experimentation. The energy of an electron is derivable from the expression $\frac{1}{2}\mu v^2 = \epsilon V$, where μ is the mass of the electron, ϵ its charge, v its velocity after falling through an electric potential of V volts.[2] We thus assume that the only effective factor in the action of the electron is its velocity, i.e., its moment and kinetic energy. We do not know what rôle, if any, is played by its electric charge, and its accompanying field. Free electrons of various velocities are available for experimentation; thus, we not only have the cathode rays of high velocities arising in discharge tubes, but electrons of smaller velocity may be obtained as thermionic emissions from heated metals. By establishing an electric field of high potential between the glowing filament (as one electrode) and a second electrode, the electrons ejected thermionically may be drawn across the intervening space. By a continuously progressive variation in the intensity of the electric field the ejected electrons may be accelerated to any convenient velocity, or what amounts to the same thing, impacts of any desirable energy may be produced.

Electrons in motion do not necessarily transmit energy to atoms during impact. This was first demonstrated by J. Franck and G. Hertz. On the contrary, electrons are readily reflected, after impact, from atoms of the noble gases and metallic vapors according to the laws of elastic impact, provided their energy, i.e., their velocity, lies below a certain limiting value. Only when the electronic velocity exceeds this critical value does it impart energy—its total kinetic energy, ϵV—to the impacted atom.

The experimental confirmation of these considerations may be accomplished along two lines: first, we may determine the extent of excitation by observation of the energy loss of the impacting atom; secondly, we may observe the result of the energy absorption by the atom, i.e., the release of energy in the form of radiation. Franck and Hertz were the first to show experimentally that an atom, upon being impacted by an electron moving with its critical velocity, experiences a change in its structure as a consequence of which it has the

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[2] An electron, accelerated by V volts, has a velocity of $v = 5.9 \times 10^7\sqrt{\text{volt}}$ cm./sec. V is also termed the "volt-velocity" of the electron.

capacity of emitting radiations. Spectroscopic examination of this emission revealed an intensely monochromatic character; in other words, a single spectral line is emitted. The kinetic energy of the electrons, obviously, has been transformed into radiant energy.

The electrical determination of the excitation, i.e., of the transfer of the kinetic energy of the electron to the atom, can be accomplished in a variety of ways; Franck and Hertz, Davies and Goucher, Foote and Mohler, Hertz, et al., have proposed special methods [3] for this purpose.

Let us now examine the phenomena obtained when the energy of the impacting electron is progressively increased. It will be observed that there are a series of such critical velocity values, and, as in the former instance, these values are not only characteristic of the gas through which the electron streams, but simultaneous with each successive decrease in energy content a radiation of definite frequency is emitted. The "excitation energy" of the atoms, whereby they are stimulated to emit radiations, are, therefore, just as truly characteristic of the respective atoms as are their emissions, i.e., their spectral lines; further, the discretion in the spectral lines finds its analogue in the sharply defined critical impact energies of the electrons. We shall see later how the quantum theory of the spectral lines explains this.

Still another remarkable phenomenon occurs when the electronic energy has exceeded a certain limiting value: positive gas ions and free electrons make their appearance in the gas. These, obviously, can originate only from neutral atoms of the gas by cleaving from them an electron, whereby the atomic residue remains as a singly charged positive ion. This ionization process evidently is contingent for its consummation upon a definite minimal energy, whose magnitude —the so-called ionization potential—is likewise characteristic of the gas in question. The ionization potential exhibits another very striking property, viz.: the dependence of its magnitude upon the chemical character of the various

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[3] See Gerlach's "Experimental Bases of the Quantum Theory."

elements. The inert or noble gases are characterized by high ionization potentials, helium having the greatest; other gases, particularly those more active chemically, possess much smaller ionization potentials.

Suppose the electronic velocity to be increased to still higher values. Here again, for certain electronic energies, new radiations in the form of spectral lines appear in addition to an intensive radiation of the characteristic spectrum of the element; finally, a second ionization of the gaseous atoms takes place, ions carrying a double positive charge making their appearance together with the singly charged ions; i.e., some atoms have lost two electrons. As already stated, there is produced, between the stages of the single and double ionizations, a new spectrum which is as truly peculiar to the chemical element as the first spectrum; the former, however, is characteristic rather of the ionized condition of the atom just as the latter is characteristic of the neutral atom.

We can summarize as follows: the highly energized conditions of the neutral atom are conditions capable of emitting line spectra, the upper limit of the energy addition resulting in the ionization of the neutral atom. The singly charged positive ion, so produced, likewise may be further energized and transformed into conditions capable of emitting radiations, the emissions being the line spectrum of the positive ion and the upper limit of stimulation the double ionization of the atom. This process is carried on, leading to a third, and even to a fourth ionization. Further increase of the electronic energy develops no essentially different phenomenon. It may be remarked, however, that successive ionization stages yielding multiple positive ions have not yet been observed for all elements.

On the other hand, with still greater recurring critical energy values, X-rays arise, each X-ray series being accompanied by, and its range limited by, an ionization process. The remarkable feature of this phenomenon lies in the production of a new set of singly charged ions and the entire absence of multiple charged ions. The energies which cause this ionization frequently exceed, even to the tenth power, the corresponding energies that stimulate optical line spectral series. Indeed, it is highly probable, in view of these phenomena, that the latter electrons do not originate from an electronic orbit, i.e., those exterior to the atomic nucleus; but rather it is more in conformity with experiment to suspect a more drastic effect upon the atomic nucleus itself, sa a consequence of which an "inner" electron may have been disrupted from it. This will be discussed more fully in Chapter XVI.

It may be inquired further: to what extent may an individual element experience these successive multiple ionizations? For the moment, no very decisive answer to this question is available, although conclusions of a more or less indirect nature suggest a reasonably plausible solution. An element can experience an *n*-fold ionization, i.e., yield variously charged ions, singly to *n*-multiple, provided it exhibits a chemical valence of "*n*." Chemism and ionization, apparently, are closely related phenomena and it is significant that the ionization energies are dependent upon the magnitudes of the energies of chemical reactions.

It will be interesting to examine more critically the stimulation of line radiation by electronic impact. In the following table are shown a series of critical electron energies together with the corresponding radiations excited by them when impacting against mercury atoms.

Excitation Energy Volts V	Observed Wave-length λ	$\frac{1}{\lambda}$	$h = \frac{\epsilon \frac{V}{300}}{\frac{c}{\lambda}}$
4.90	2,536.7	39,410.4	6.57×10^{-27}
6.73	1,849.6	54,064.5	6.54
8.64	1,435.6	69,657.5	6.52
8.86	1,402.7	71,290.7	6.53
9.79	1,268.9	78,809.9	6.54
10.38	1,187.88	84,176.8	6.49

A survey of the data in columns 1 and 2 will disclose that, generally, greater excitation energies are required to stimulate an atom to the emission of the shorter wave-lengths. This inverse relationship of energy to wave-length is corroborated by similar measurements made upon many other atoms. If, in column 3, we substitute c/λ for λ—that is, if we compare the frequencies ν of the emitted radiations rather than their respective wave-lengths λ—it will be observed that these are directly proportional to the respective "exciting" electron energy. The magnitude of the proportionality factor involved in this relation is found to be sensibly constant and applicable not only to all atoms but to all radiations thus far measured. It is the same for frequencies in the infra-red and ultra-violet ranges as well as for the visible portions of the spectrum, and—with due regard for certain peculiar characteristics—it may be extended to frequencies falling within the range of X-rays. Numerically, this constant is equal to 6.54×10^{-27}, as evaluated from the relation (column 4)

$$h = \frac{\epsilon V/300}{c/\lambda}.$$

It is expressed as erg secs., and obviously partakes of the nature of energy. This factor, called Planck's constant, or briefly Planck's h, is a natural constant, the universal constant involved in all molecular and atomic inversions.

In the light of experimental data, as synopsized in the foregoing table, we may formulate a reasonably correct interpretation regarding the mechanism of the conversion of the kinetic energy of the impacting electron into radiant energy. According to the quantum theory the energy content of a monochromatic radiation of frequency ν $(= c/\lambda)$ is expressed by the product of the given frequency ν into Planck's constant h, i.e., $h\nu$. The intensity of the radiation, however, is measured by the number of energy "quanta" $h\nu$ present in the radiation, or $J = N \cdot h\nu$. Obviously, from the viewpoint of the quantum theory, the emission of monochromatic radiation of frequency ν postulates a definite electronic energy capable of stimulating this emission. Or $h\nu = \epsilon V$ in which ϵV designates the previously described minimal energy, the critical energy, that may be absorbed by the atom. For mercury vapor this critical excitation potential was found experimentally to be 4.9 volts; evaluated for the observed monochromatic emission = 2,536.7 Å., by means of the general relations $V = h\nu/\epsilon$ and $\nu = c/\lambda$, it was found to be 4.86 volts, a remarkable agreement with the experimental value. In this manner Franck and Hertz established in 1914 the experimental basis of the quantum theory, which even today exerts a fecund influence upon the greater number of physical investigations. It was especially noted that the impact of 4.9 volt-electrons (as the energy is customarily expressed in briefer terminology) did not ionize the mercury atom and that radiation results, therefore, from more highly energized atomic conditions which are not distinguishable electrically from the normal atom.

The other wave-lengths λ cited in the foregoing table were not obtained in so direct a manner by spectroscopic measurement as a result of the electron velocities given in the first column. It was possible to show merely the presence of a new ultra-violet emission for each critical velocity given in the first column. That the observed emissions have the wave-lengths specified in column 2 follows from the fact that they correspond to the known spectral lines of mercury—and are computable according to the relationship given above from the measured electron energies. Undubitably, this cannot serve as proof for Bohr's assumptions. As a matter of fact, American physicists for a long time rejected this explanation as proposed by Franck.

Within recent years, however, Gustav Hertz has carried out a series of experimental investigations which confirm definitely the general validity of Bohr's equation and Franck's explanation of excitation by electronic impact, viz.: that the production of new spectral lines results suddenly and they are sharply defined as soon as the excitation energy is reached and exceeded.

It is evident, therefore, that electrons moving with a certain definite velocity transfer their entire energy to an impacted atom whereby the latter is transposed into a condition of higher energy content capable of emitting radiations. The "life-period" of this new atomic state is characterized by its extremely brief duration. The atom spontaneously and of its own power reverts readily and rapidly to its original condition; during this reversion, the energy, previously absorbed by the atom and which occasioned its transformation, is disengaged as a monochromatic electromagnetic radiation. The spontaneity of this reversion, its concomitant liberation of energy, and its absolute independence of the influence of exterior forces are demonstrated by the positive experimental results recently announced by W. Wien. In these experiments positive rays were projected into such extremely high vacua that the "excited atomic conditions" would emerge from the discharge in such a way that collisions with all other atoms were eliminated. Under such conditions the emission of radiant energy by the atoms is easily observable. In addition, these experiments have made possible the direct computation of the life period of the transformed atom, that is, the time interval actually spent by the original atom in the "excited" or stimulated condition. This proves to be of extremely small duration, somewhat of the order of magnitude 10^{-8} sec. Previous estimations of these life periods were based upon purely indirect data.

The theory of the atom, as advanced by Bohr, proposes a very precise viewpoint to explain the variations in atomic structure due to the absorption of energy. The theoretical developments which prompted Bohr to the enunciation of his theory are treated by A. Landé in "The Development of the Quantum Theory." We shall confine ourselves, accordingly, to a brief presentation of the mechanism of atomic changes as ideally conceived in the light of Bohr's postulates. Thus, when an atom experiences an excitation one of its electrons leaves its normal orbit and becomes localized in another orbit farther removed from the atomic nucleus, the abstracted electron remaining nevertheless so firmly bound to the positive nucleus that the atom still persists exteriorly as an electrically neutral individual. On the quantum theory all the changes arising within an atom as a result of electronic impact must be induced, likewise, by the energy of electromagnetic radiation, provided the frequency ν of the radiation is so chosen that its quantum $h\nu$ is equal to the electronic energy ϵV which the atom is capable of absorbing selectively. Radiation can be effective only when it is absorbed. This is a universal axiom of energetics. Absorption of radiation takes place, however, only when its quantum $h\nu$ is equal to that critical electronic energy which the atom by virtue of its structure is disposed to absorb. In other words, whenever an atom is convertible into a more energetic form through the agency of a definite electronic energy ϵV, the same net result must be attained through the instrumentality of a radiation whose frequency $\nu = \epsilon V/h$. As a consequence, the atomic condition brought into being by the absorption of a definite radiation quantum will disintegrate eventually with the simultaneous emission by it of radiation of the same frequency. This phenomenon is termed "resonance radiation." The purely monochromatic character of resonance radiations was first demonstrated by R. W. Wood. The equality of the absorbed and the emitted energies subsequently was verified for helium atoms by F. Paschen, for sodium by Wood and Dunoyer, and for mercury by Gerlach. (For details see Chap. XVII.)

It is possible also, in certain cases, to demonstrate by purely chemical methods the transition of an atom from its normal form to a more highly energized condition. This is quite evident inasmuch as the changed atom, by virtue of its higher energy content and attending alteration in the electronic configuration about the nucleus, can exhibit a certain reaction capacity which is foreign to it while in its normal condition. Such processes lie in the scope of "Photochemistry." Photochemical processes, thus far studied quantitatively, are concerned almost entirely with molecular reaction, the simplest cases being those of "double" atoms (Homopolar molecules), as, e.g., iodine I_2, hydrogen H_2, and the ozonizing of oxygen, etc. Purely atomic photochemical phenomena have not yet been observed directly. Physically, the existence of such reaction products is easily conceivable. Unquestionably "double atoms" (molecules) of such elements which yield monatomic vapors are of this type; among them are the molecules of mercury, of sodium and others. Their existence is confirmed by their respective spectra. Mercury vapors, rendered radiant by electric stimulation, emit not only a line spectrum, but a band spectrum as well. Band spectra, it will be remembered, are peculiar to molecules and not to atoms.

Besides revealing the existence of these more highly energized atomic states, the electronic impact method has achieved still another noteworthy experimental success. By its means, J. Franck has observed that many atoms, e.g., atoms of helium and of mercury, may absorb certain definite electronic energies and yet not undergo a concurrent transformation into a more active (i.e., radiating) condition. The net effect of such an action consists in the absorption of the electronic energy and the formation of an atomic state of a higher energy content and of a greater life-period; the new form cannot be reconverted into the parent normal atomic state either by its own accord, by the emission of radiation or by any other known process. Such atomic states are known as "metastable states." Their fuller significance will be discussed in a later section.

Attention may now be directed momentarily to a phenomenon to which reference has already been made in the earlier part of the chapter, viz.: the elastic reflexion observed in the so-called noble gases for electrons of low velocity. It was observed, first by C. Ramsauer and later by H. F. Mayer, that atoms of argon were extremely permeable to low-speed electrons. This result is usually formulated in the statement the "effective cross-section" which is proportionate to the absorption, scattering, and reflexion of electrons, decreases progressively with a decreasing velocity of the electrons. Subsequent experiments by G. Hertz and M. Rusch confirmed this permeability and lack of reciprocal influence between the electronic orbits and the slow-speed electrons; H. Spooner, Minkowski, and Ramsauer also noted a similar effect for helium, neon, xenon, krypton, and metallic vapors. Theoretical explanation of this phenomenon has been attempted by Fr. Hund. Slow-speed electrons within the field of force about an atom should be tractated into the nucleus. Such an attraction, however, would postulate a release by the electron of more energy than is actually possessed by it in the form of kinetic energy. "There is nothing left to it but to pass directly through the atom in a straight line." The "permeability velocities" calculated on this theoretical basis are in fair accord with the experimental velocities. The minimum effective cross section for slow-speed electrons ought to be, obviously, a universal property of atoms. Reference is made to these investigations at this point because their results are of great importance to many effects arising from the impact of slow electrons upon inert gases. The theoretical interpretation, as far as the atomic theory is concerned, may be considered as consistent, but perhaps as not yet final.

We are inclined to believe that the mechanical interpretation of our deliberations concerning the impact of electrons upon atoms will have to be abandoned. This applies also to the atomic collisions, "excited" as well as "non-excited." The stoppage of an electron, like any impacting wave, may be considered mathematically as a superposition of frequencies (Fourier's Analysis) and the effect of such an impact should be understood as a resonance of one or more of these frequencies with corresponding frequencies within the atom. The material theory of impacts of atoms and electrons would then be merely a schematic formulation of the electromagnetic phenomena in the superposition of electromagnetic vibrations. We mention this merely in passing.

A more extensive and a more fundamental aspect is imparted to our considerations of the subject matter by the examination of the spectral absorption of gases and vapors. In the foregoing paragraphs our attention was focused primarily upon the excitation of normal atoms to line emissions. We considered there the mechanism of the action whereby a normal atom may be converted into atomic states of greater energy content, E_1, E_2, E_3, $\cdots$, which states, in turn, are capable of reversion to the original normal condition E_0 by the emission of radiation of the appropriate frequencies, ν_1, ν_2, ν_3, etc., and whose energy differences $E_1 - E_0$, $E_2 - E_0$, $\cdots$, etc., are mutually so related according to Bohr's equation that

$$\nu_1 = (E_1 - E_0)/h;\ \nu_2 = (E_2 - E_0)/h;\ \cdots;\ \text{etc.}$$

These are by no means all the possible emission or spectral lines of a normal atom, but only a specified number of them which collectively constitute, and are termed, a series. A spectral line series results, therefore, when a number of excited states of various energy contents are reconverted to the same final atomic condition of smaller energy content. Should this final state happen to be the normal condition of the atom, then the series so produced is termed the "principal spectral series" of the element in question. It is patent, also, in the sense of the quantum theory that energy absorption must compensate in some manner for these emissions. When, therefore, an atom experiences a transition from one condition E_n to another E_0 with the simultaneous emission of the frequency ν_n, the absorption of this latter frequency will reconvert the atomic state E_0 to the initial state E_n. Such a phenomenon is termed "absorption." For a given frequency ν_n to be absorbable by a gas or vapor it is requisite, therefore, that the given frequency be likewise an emission frequency of the substance in question; further, the proper initial state E_0, capable of absorbing the frequency, must be present in the gas. A gas, activated by no energy whatever, will absorb only such frequencies capable of being taken up by its normal atom E_0. Absorption spectra of gases and vapors give rise, therefore, to that series of spectral lines previously designated as the principal series. Knowledge of this series is of great significance since it indicates directly to us the several energy states into which an atom can be transformed; and, further, it plainly reveals a very important property of the element in question. Knowledge of the relative energy contents of these states permits reasonable inference concerning the forces operative within an atom and ultimately concerning atomic structure itself. Of especial interest is the "boundary" of the principal series. Mention has already been made of ionization potentials earlier in this chapter. It is not possible technically to determine these potentials directly for all elements by electrical methods. Determination of these magnitudes is possible by optical means if the boundary of the principal series is known. The maximum energy absorbable by a normal atom is that which can ionize it, that is, convert it into an ion by the complete separation from it of a "photoelectron." Obviously, this ionization stage must coincide, of necessity, with the upper limit of the absorption series. The latter is related to the ionization energy according to the expression $E_j = h\nu_\infty$, wherein ν_∞ represents the limiting frequency of the absorption spectrum and likewise the greatest emission frequency of the neutral atom.

We may now ask: how will an atom deport itself toward a still greater frequency, i.e., toward a greater energy absorption? We may conceive reasonably that, as a result of the absorption of its limiting frequency, an electron has been withdrawn to such extreme distance from its atom that it no longer lies within the sphere of electric attraction emanating from the atomic nucleus. Since the limiting frequency just suffices for this, the outcome of this action will be the production of an ion and a free electron cleaved from it. Experiment has shown, also, that greater frequencies than this limiting frequency are absorbable with the production of a continuous absorption spectrum of these higher frequencies in addition to the series of the individual absorption frequencies.

The excess energy appears as kinetic energy of the liberated electron. The maximum frequency of the absorption line spectrum corresponding to the ionization energy (see above) is therefore simultaneously the lowest frequency of the continuous absorption spectrum attached to the series. This fact has been established repeatedly in the laboratory and observed particularly in the spectra of stars.

In addition to the determination of the principal series of an atom, there are other phenomena that accentuate the importance of the absorption method. Thus, the perplexing problem of the formation of molecules in monatomic vapors—already referred to—is by its aid readily explainable. In the case of mercury vapor, an absorption band has been observed repeatedly by several investigators, which is formed entirely independent of simultaneous excitation of the mercury atoms. If we apply to band spectra considerations similar in principle to those extended to line spectra, and if we bear in mind, moreover, that band spectra are always peculiar to, and characteristic of, molecules, then obviously the occurrence of these bands indicates decidedly the presence of molecules in the normal and non-activated mercury vapor. Stated otherwise, mercury vapor cannot be regarded as completely monatomic in structure. Its preponderant monatomic character is evidenced optically by the appearance of absorption series lines. The nature of such molecules is not explainable easily by chemical means due to the paucity of their number. It is possible, however, to make rather definite statements about them based upon optical data. In the first place the position of the bands in the spectrum is significant. The principal absorption band in mercury vapor is situated very closely to the first absorption line of the mercury atom. The "absorbing" atom within the mercury molecule apparently absorbs very nearly the same frequency as does the "free" atom and in addition many of the adjacent frequencies. Due to the influence of the second atom in the molecule, the structure and the distribution of the forces within the first atom will be modified slightly. The union of the two mercury atoms accordingly will be very loose. The intensity of this molecular union is determinable likewise by optical means. One would anticipate, for progressively elevated temperatures, that the mercury molecules, Hg_2, dissociate proportionately into their constituents Hg + Hg, and that the intensity of the absorption will decrease with the diminution of the mercury Hg_2 molecules. Franck and Grotian quantitatively investigated this gradual vanishing of the absorption bands with rise in temperature and from the data thus obtained they calculated the heat of dissociation of the mercury molecules to be about 1,000 cal. This represents, indeed, a very small energy, especially so when compared to the energies of other chemical reactions. This corroborates the conclusion previously drawn from the position of the spectrum.

The behavior described above is not peculiar to mercury alone. Thallium and indium as well as the noble gases and the alkali metals, and presumably also several alkali metals among themselves, exhibit characteristics indicative of double molecules. Definite and precise conclusions regarding the latter's band and absorption are still lacking.

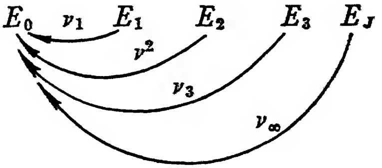
A few remarks, more or less general in nature, may be made at this point regarding the origin of band spectra. The fundamental principles and ideas, upon which are based our knowledge of band spectra, have been elaborated by Heurlinger and Lenz; more recently these were further developed and amplified, particularly by A. Kratzer. Consider two atoms so combined as to form a molecule. Several frequencies are possible to this molecule. Firstly, there are the absorption and emission frequencies arising from the stimulation of one of the constituent atoms, whereby an electron is removed from its normal orbit to a higher energy level. Two additional types of frequencies are possible: the vibration resulting from the mutual motion of the atoms within the molecule usually termed vibration frequencies; and the mutual rotations of the constituent atoms about one another produce other frequencies, termed the "rotational frequencies." According to the quantum theory these latter two frequencies should each be characterized by only one series of discrete values. In this manner it has become possible to explain band systems, e.g., the band spectrum of the nitrogen molecule. The large intervals in the bands correspond to the oscillation frequencies, while the fine structure of the individual intervals is due to rotational frequencies.

The reasonableness of this viewpoint is verified especially in explaining the infra-red absorption spectra of water vapor which likewise are due to such oscillation frequencies. This phase will receive more thorough discussion in Chapter XVIII. An application of the theory has already been discussed in Chapter II, in connection with the demonstration of the isotopic character of chlorine by spectroscopic methods.

In addition to the several "excited" states of atoms occasioned by the absorption of energy, other atomic conditions capable of emitting radiations are also possible. Critical examination of the line spectrum of an element will disclose a rather large number of such possible conditions. Excitation of the normal atoms yields—apart from possible metastable conditions—only such atomic states that are capable of reversion to the parent normal atom with simultaneous emission of definite radiation. If we designate the original atomic state, or its energy content, by E_0, and the several excited states by E_1, E_2, E_3, respectively, then, obviously, the frequencies of the principal series may be represented by

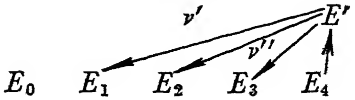
$$\nu_1 = \frac{E_1 - E_0}{h}; \qquad \nu_2 = \frac{E_2 - E_0}{h}; \qquad \nu_3 = \frac{E_3 - E_0}{h}, \qquad \text{etc.}$$

or



It is well within reason to assume, further, that energy changes involving the transposition of the excited state to another of smaller energy content (other than the parent state) likewise take place with the emission of the appropriate radiation. Thus, the atomic state E_2 may transform to E_1 rather than revert to the normal E_0.[4] Under ordinary circumstances this does not occur; under special conditions, however, e.g., under the influence of very strong electric fields, transitions of this type appear to occur. We refer the reader to the many theoretical discussions of this topic, upon which we shall not enter in detail.

The numerous other lines observable in a spectrum doubtless owe their origin to transitions involving other possible energy "levels" of the atom. Spectral analysis, due to a considerable extent to the work of F. Paschen,[5] has made possible the determination of the several atomic states of varying energy content for a large number of atoms. That Bohr's frequency relation plays an important rôle here also is indicated by the Ritz "combination-principle." We will assume the existence of an energy state E', apart from the series E_0, E_1, E_2, etc. Normally, the atom E_0 will not be excited to transform directly to E'. Two distinct spectral lines may be associated with the transitions $E' \to E_1$ and $E'_4 \to E_2$. It follows, consequently, that the difference between the frequencies ν' and ν'' arising respectively from these conversions must bear a definite relation to the energy difference of the two states E_1 and E_2, i.e., to $E_2 - E_1$. More definitely put, $(E' - E_1) - (E' - E_2) = E_2 - E_1$. Schematically, this may be presented as



Similarly, energy transformation corresponding to $E_3 \to E'$ and $E_4 \to E'$ are possible with the accompanying emission of

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[4] For the related problems the reader is referred to A. Landé's "Forschungsberichte," Vol. 6; N. Bohr (Vieweg & Son) and A. Sommerfeld, "Atomic Structure and Spectral Lines."

[5] F. Paschen and R. Goetze, "Line Spectra" (published by J. Springer, 1922).

their respective frequencies, ν''', ν^{IV}. A new series of spectral lines, based upon the energy state E', arises accordingly from such energy transpositions.

Considerations such as these lead to an inevitable consequence which may be discussed in connection with a previously cited phenomenon. Reference has already been made to the concept "resonance radiation" in the early part of this chapter. Absorption of the frequency ν_1 of the first line of the principal series transforms an atom, as stated, to the more highly energized condition E_1; conversely, for a subsequent reversion of the atom from E_1 to E_0, this absorbed radiation is disengaged and emitted as a monochromatic vibration of the same frequency ν_1. In precisely the same manner, absorption of the frequency ν_2 alters the atomic state from E_0 to E_2. However, reversion from E_2 to E_0 results in the remission not only of the frequency ν_2, the spectrum showing marked evidence of the first line ν_1 together with ν_2. The following exposition may prove helpful to a better understanding of this phenomenon. According to our previously accepted notion, the emission of the frequency ν_1 presupposes the formation of the atomic state E_1. This, however, is formed neither by absorption of the frequency ν_2, nor is it possible for the atom to be transformed directly from E_2 to E_1. It is conceivable, however, that an atom may not revert directly from the higher to the lower state, i.e., go directly from E_2 to E_0. Indirectly this may result as follows: E_2 may transform into the spectroscopically

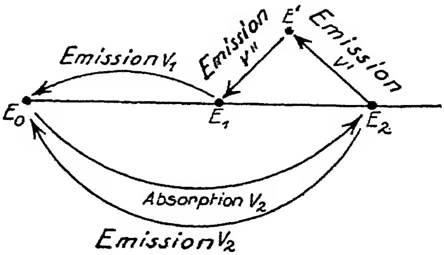

FIG. 34.

known state E' with the simultaneous emission of an appropriate frequency ν'; this intermediate state, in turn, will emit a frequency ν'' and be converted into E_1; finally, E_1 will revert in the normal manner to E_0 with its characteristic frequency emission of ν_1. The appearance of the frequency ν_1 in addition to the normally expected frequency ν_2, as a result of stimulation with ν_2, is thus readily explainable. Unfortunately, this phenomenon has been investigated but once—in the case of sodium—and this was not marked with sufficient thoroughness and accuracy. In view of such meager evidence, no very positive assertions can be made regarding the existence and appearance of such intermediate frequencies ν' and ν''. It is possible that such intermediate lines may lie in the infra-red spectrum which are not very accessible spectroscopically. There is, however, still another possibility whereby these emissions may be produced. The transition from E_2 to E_1 cannot possibly occur with simultaneous emission of a definite frequency, for the spectral line corresponding to this change would be observable under such condition and its intensity would be of the same order as that of the frequency ν_1. It is easily conceivable, however, that this change may take place without any characteristic radiation under the influence of exterior force, e.g., during collisions of E_2 atoms with atoms of different energy contents, the liberated energy $E_2 - E_1$ appearing in some other form, as, for example, kinetic energy. The possibility of such reconversions has been proved experimentally. We are not in a position to state which of the two possible mechanisms is correct. Both are readily understandable and compatible with our present views.

The work of Franck and his co-workers on the various energized states of helium has been thoroughly corroborated recently by direct spectroscopic measurements in the extreme ultra-violet. Lyman successfully measured the principal emission series of helium. For each spectral line there is a critical excitation energy whose magnitude is related to the frequency of the line ν by the expression $h\nu = \epsilon V$. We have remarked in a previous section that helium exhibits a transition of the normal atom into a metastable form in addition to the usual change of the normal atom to the excited state E_n. No definite radiation corresponds to this change since the metastable condition reverts to the normal form without emission. The following table presents a summary of these observations.

Spectral Lines Observed by Lyman in Å.	Calculated Excitation Energy $V = h\nu/\epsilon$	Observed Excitation Energy	Remarks
Not observed	—	19.65	Metastable state (see below)
600.5	20.55	20.45	Only present in strong electric field of the impacting electron
584.4	21.12	21.10	Principal series
537.1	22.97	22.8	
522.3	23.62	Not measured	
515.7	23.92		
502 (series limit)	24.5	24.5	Ionization

The boundary of the principal series corresponds here as in all other measurements to the ionization energy.

CHAPTER XII

THE HYDROGEN SPECTRUM

The extreme simplicity of the spectrum of hydrogen has attracted attention since the beginning of systematic spectroscopic investigation. There are fewer lines in it than in the spectra of other elements, these becoming more and more closely spaced toward the violet end of the visible spectrum while in the long wave ultra-violet region they follow upon one another so rapidly that they form an almost continuous band of low intensity. These lines constitute the well-known Balmer series (see below).

Direct measurement of the ultra-violet and infra-red regions of the hydrogen spectrum revealed the presence in them of still other hydrogen lines. Thus, Lyman observed a line series in the extreme ultra-violet (Lyman series) whose habitus displayed a remarkable similarity to the spectral line series previously noted in the visible portion of the spectrum. Somewhat later, another analogous series was discovered in the infra-red region (Paschen series). The general structure of the hydrogen spectrum may be depicted, accordingly, as in Figure 35.

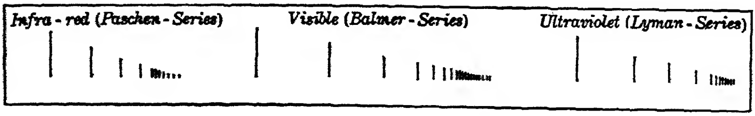

FIG. 35.

In discussing these extremely orderly phenomena we will disregard entirely the historical sequence of their discoveries and we will attempt, in the light of our present experimental knowledge, an explanation of the theory of spectral series as applicable in this case. Obviously, we must bear in mind that this may be accomplished only under very special conditions, conditions which lend themselves rarely to actual practical experimentation.

We may ask firstly: does hydrogen (we refer here to atomic hydrogen) emit only this one spectral line series, or are other series known to occur? Stimulation of hydrogen, i.e., the impartation of energy to its atom, may be brought about chiefly by elevation in temperature. Since experimental difficulties very frequently make this type of stimulation very impracticable and prohibitive, recourse is had to the method of electronic impact which occurs necessarily in every Geisler tube. The first notable result, subsequent to stimulation, is the invariable emission, by the hydrogen atom, of that line series which has the shortest wave-lengths. This fact may be interpreted readily in terms of atomic stability. Due to the effectiveness of atomic stability small energies cannot modify the normal form of the atom, that is, produce from it a "radiating atom." The relative ease with which an atom may be stimulated is a direct measure of its stability, and particularly, it may be stressed here, a measure of its chemical stability. The greater the excitation energy necessary for stimulation, the less reactive the atom in a chemical sense. The large excitation energies of the inert gases, especially of helium and neon, and the small energies of the alkalies may be cited as typically illustrative examples.

In the case of hydrogen, therefore, the Lyman series—strictly speaking, only the first line of the series—corresponds to the lowest excitation state of the atom. With increasing excitation energies the several lines of the Lyman series arise in successive stages. These measurable energies are related to the corresponding wave-lengths of the emitted lines according to an empirically determinable formula,

$$\lambda E = 19.6 \times 10^{-17} = \text{Constant},$$

where λ is the wave-length of the emitted radiation and E the energy requisite for its emission. The constant numerically is equal to the product of the velocity of light c times Planck's constant h, viz.: $3 \times 10^{10} \times 6.53 \times 10^{-27}$. We already are familiar with the quantum interpretation from principles laid down in Chapter XI, viz.:

$$\lambda E = h \cdot c; \qquad E = h(c/\lambda) = h \cdot \nu.$$

Since the normal state of the atom is restored following its stimulation by impartation of energy to it and the subsequent emission of radiation, it is apparent that the emission process consists essentially in the disengagement of the absorbed energy which reappears in the form of emitted radiation.

We may now ask: when will the Balmer series arise, whose wave-lengths require a much smaller excitation energy, provided, of course, that Bohr's frequency ($E = h\nu$) relationship is valid here also? Since these smaller energies do not stimulate the normal hydrogen atom, we must conclude, of necessity, that the Balmer series is not proper to the normal hydrogen atom but characteristic rather of some definite atomic state which is so unstable that even very small energies are capable of altering it by transforming it into another state capable of emitting radiation.

It was recognized, in turn, that this definite state of the hydrogen atom, which can be stimulated to the emission of the Balmer series, may be formed, likewise, by the same energy amount which excites the normal atom to the emission of the first line of the Lyman series.

But what about the Balmer series itself? As in the Lyman series there is a gradual succession of one line upon another and for each line the product of the requisite excitation energy times the respective wave-length is constant and again equal to the product hc.

A similar phenomenon recurs for the Paschen series and again for other successive series observed to exist in the long waved portions of the infra-red spectrum and which have been measured successfully during recent years in America. The Paschen series can arise only when the normal atom has been stimulated previously to the emission of the first "Lyman" state, and this, in turn, only when the first "Balmer" state has been formed. Under such conditions, the normal atom has been transposed to that definite atomic state which can be stimulated directly to the emission of the Paschen series by the absorption of very small energy amounts.

The general conclusion of these considerations, that a given spectral series is characteristic not merely of a specific atom but likewise of a definite physical state of it, may be represented graphically (Fig. 36). We shall indicate the several energy levels to which a normal atom can be elevated upon excitation with the appropriate energy. Of all the possible states, or energy levels, we will group those capable of reversion to the same initial state upon liberation of the absorbed energy in the form of monochromatic radiation. Such a group forms a "series." The liberation of energy by the atom as it reverts from a higher to a lower energy level proceeds in the form of a monochromatic radiation.

However, before taking up this graphic presentation it will behoove us to consider (1) the empiric-theoretic explanation of spectral series according to Balmer and (2) the calculation of the wave-lengths of the lines from the point of view of the atom and quantum theories according to N. Bohr.

Balmer Series

The particular characteristic sequence of the lines in the hydrogen spectrum suggested to J. J. Balmer of Basle that this was representable by means of a formula. Accordingly, he showed in 1885 (Wied. Ann., Vol. 25, p. 80) that the wave-lengths of the first four lines (H_α, H_β, H_γ, H_δ) measured with great accuracy by Ångström may be expressed by the very simple equation

$$\lambda_m = k\frac{m^2}{m^2 - 2^2}; \qquad k = 3{,}645.6 \text{ Å.},^1$$

where λ denotes the wave-length and m has the value 3, 4, 5, 6 for the lines H_α, H_β, H_γ, H_δ respectively and k is a constant. He surmised at the same time that this formula is valid for other hydrogen lines which must be so situated, according to this formula, that their wave-length difference progressively becomes smaller; further, there are no hydrogen lines whose λ value is smaller than 3,645.6 Å. (when $m = \infty$, $\lambda = k$).

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[1] 1 Å. = Ångström unit = 10^{-8} cm. = 10^{-7} mm.

The wave-length $\lambda = 3{,}645.6$ is therefore the limiting frequency or head of the series. Subsequently, lines were observed by Huggins in the spectra of stars which corresponded to the lines calculated by Balmer for values of $m > 6$ and up to $m = 15$.

Balmer realized completely the significance of this discovery as is indicated by his characterization of k as a fundamental number proper to the hydrogen atom and his further suggestion that there is such a correspondingly fundamental number for other elements, the numbers in each case being associated directly with the structure of the emitting atom, perhaps with its atomic weight.

If we remember that wave-lengths are related to their respective frequencies and the velocity of light according to the expression $\nu\lambda = c$, we will obtain for the frequency ν_m (instead of wave-length λ_m) the value

$$\nu_m = \frac{c}{\lambda} = \frac{c}{k} \cdot \frac{m^2 - 4}{m^2} = \frac{c}{k}\left(1 - \frac{4}{m^2}\right); \qquad m = 3, 4, 5, 6, \cdots$$

or

$$\nu_m = \frac{4c}{k}\left(\frac{1}{2^2} - \frac{1}{m^2}\right); \qquad m = 3, 4, 5.$$

In experimental spectroscopy it has been found more convenient and preferable to use in place of $\nu = c/\lambda$ the simple reciprocal of the wave-length $n = 1/\lambda$, called the wave number, i.e., the number of wave-lengths in 1 cm. Therefore,

$$n_m = \frac{4}{k}\left(\frac{1}{2^2} - \frac{1}{m^2}\right),$$

$$n' = N\left(\frac{1}{2^2} - \frac{1}{3^2}\right), \qquad N = \frac{4}{3{,}645.6 \times 10^{-8}\ \text{cm.}},$$

$$n'' = N\left(\frac{1}{2^2} - \frac{1}{4^2}\right), \qquad N = 109{,}700\ \text{cm.}^{-1}, \text{ approximately,}$$

$$n''' = N\left(\frac{1}{2^2} - \frac{1}{5^2}\right),$$

etc.

are the wave numbers of the Balmer series of the hydrogen atom.

In exactly the same way we may represent the other series of the hydrogen spectrum. The formulas expressing the relationships of these series are as follows:

Lyman series....... $n = N\left(\frac{1}{1^2} - \frac{1}{p^2}\right)$, $(p = 2, 3, 4, \cdots)$,

Balmer series........ $n = N\left(\frac{1}{2^2} - \frac{1}{m^2}\right)$, $(m = 3, 4, 5, \cdots)$,

Paschen series...... $n = N\left(\frac{1}{3^2} - \frac{1}{k^2}\right)$, $(k = 4, 5, 6, \cdots)$,

Successive infra-red series..........

$$\begin{cases} n = N\left(\frac{1}{4^2} - \frac{1}{l^2}\right), \\ (l = 5, 6, 7, \cdots), \\ n = N\left(\frac{1}{5^2} - \frac{1}{j^2}\right), \\ (j = 6, 7, 8, \cdots), \end{cases}$$

etc.

LYMAN SERIES (ULTRA-VIOLET)

$$\nu = N\left(\frac{1}{1^2} - \frac{1}{p^2}\right), \qquad p = 2, 3, 4, \cdots, \qquad N^{*2} = 109{,}677.69.$$

	λ calculated Å.	λ observed Å.
$p = 2$...........................	1,215.68	1,216.0
3...........................	1,025.73	1,026.0
4...........................	972.55	972.7
	etc.	

BALMER SERIES

$$\nu = N\left(\frac{1}{2^2} - \frac{1}{m^2}\right), \qquad m = 3, 4, 5, \cdots.$$

m =	λ calculated Å.	λ observed Å.	Line
3	6,562.80	6,562.80	H_α
4	4,861.38	4,861.33	H_β
5	4,340.51	4,340.47	H_γ
6	4,101.78	4,101.74	H_δ
7	3,970.11	3,970.06	H_ϵ
—	—	—	
15	3,712.01	3,711.98	
16	3,703.89	3,703.86	
—	—	—	
30	3,662.29	3,662.21	
31	3,661.25	3,661.21	
—			
∞ limit of series			

[*2] According to F. Paschen. See Paschen-Goetze, "Spectral Lines" (Springer, 1922).

PASCHEN SERIES

$$\nu = N\left(\frac{1}{3^2} - \frac{1}{k^2}\right), \quad k = 4, 5, 6, \cdots.$$

	λ calculated Å.	λ observed Å.
$k = 4$	18,751.35	18,751.3
5	12,818.32	12,817.6
	etc.	

Balmer's discovery served as the foundation upon which modern physical spectral analysis was developed theoretically by Rydberg and Ritz and experimentally by Kayser, Runge, Paschen, etc., which has been formulated satisfactorily, at least for the present, in Bohr's theory of spectral emission and atomic structure.

Bohr's Calculation of the Hydrogen Lines

We will discuss finally the principles upon which Bohr has developed his theoretical treatment of the emission problem. The fundamental assumptions are somewhat as follows. An atom—any atom taken at random—may be considered, according to Bohr, primarily as a mechanical system in which one body rotates about another, e.g., a single (negative) electron about a singly charged positive atomic core. The atom of hydrogen thus presents the simplest case imaginable, for in it its sole electron rotates about an atomic nucleus having a unit positive charge, the so-called proton. The laws applicable to such a system are the mechanical law of rotational motion and Coulomb's law expressing the attraction between two opposite charges. If μ is the mass of the rotating electron, r the radius of its orbit upon which it is moving with an angular velocity w, the centrifugal force acting upon the electron is

$$F = \mu r w^2. \tag{1a}$$

Further, let ϵ designate the charge upon the nucleus and electron respectively while at the distance r; Coulomb's attractive force is then expressible as

$$C = \epsilon \cdot \epsilon / r^2 = \epsilon^2 / r^2. \tag{1b}$$

For the atom to retain its permanency and stability its system must be in equilibrium with respect to these two forces; that is, C must balance F, or $C = F$, i.e.,

$$\mu r w^2 = \epsilon^2 / r^2. \tag{1}$$

Thus for the kinetic treatment of the problem. But we must consider also the energies involved since the energy question stands out prominently as an important factor in the problem of excitation and radiation.

The kinetic energy of a rotating electron is

$$E_{\text{kin.}} = \tfrac{1}{2}\mu r^2 w^2, \text{[*3]} \tag{2a}$$

and its potential (Coulomb's) energy

$$E_{\text{pot.}} = -\, \epsilon^2 / r. \tag{2b}$$

From (1) we obtain the relation

$$\mu r w^2 = \epsilon^2 / r^2,$$
$$\mu r^2 w^2 = \epsilon^2 / r.$$

The total energy content is thus the summation of its kinetic and potential energies, or $E_{\text{kin.}} + E_{\text{pot.}} = \frac{1}{2}\mu r^2 w^2 - \epsilon^2 / r$; and since, according to (1), $\epsilon^2 / r = 2 \cdot \frac{1}{2}\mu r^2 w^2$, this becomes $\frac{1}{2}\mu r^2 w^2 - 2 \cdot \frac{1}{2}\mu r^2 w^2$. In other words, it is equal to the kinetic energy taken negatively,

$$E = -\, \tfrac{1}{2}\mu r^2 w^2. \tag{II}$$

[*3] $\frac{1}{2}\mu v^2 = \frac{1}{2}\mu r^2 w^2$, since $v = rw$.

The negative sign in itself is immaterial and of little significance since it is only the energy differences and energy changes that come into consideration from a physical point of view.

The moment of momentum mvr of the electron with an angular velocity w ($v = rw$) is

$$J = \mu r^2 w \tag{3a}$$

or, for a complete revolution of the electron (upon the orbit 2π),

$$J_0 = 2\pi\mu r^2 w. \tag{3b}$$

On the quantum theory this moment of momentum is equal to a whole multiple of Planck's constant h,

$$J_0 = h, 2h, 3h, \cdots, nh. \tag{3c}$$

h or a multiple of it, therefore, are the only values possible for the moment of momentum; or, generally, we may write

$$2\pi\mu r^2 w = nh. \tag{III}$$

From (II) and (III) we may evaluate respectively the unknown values of r, the radius of the orbit described by the electron about its nucleus, and of w, the electron's angular velocity upon this orbit.

$$r = \frac{n^2h^2}{4\pi^2\mu\epsilon^2},$$

$$w = \frac{8\pi^3\mu\epsilon^4}{n^3h^3}.$$

These two expressions contain only known atomistic magnitudes μ, ϵ, and h. Moreover, since n can be only a whole number according to the basic postulate adopted, only discrete orbits are possible having the following radii:

$$\begin{aligned}
n &= 1; & r_1 &= \frac{h^2}{4\pi^2\mu\epsilon^2}; & w_1 &= \frac{8\pi^3\mu\epsilon^4}{h^3}; \\
n &= 2; & r_2 &= \frac{4h^2}{4\pi^2\mu\epsilon^2}; & w_2 &= \frac{8\pi^3\mu\epsilon^4}{8h^3}; \\
& & &= 4r_1 & &= \tfrac{1}{8}w_1 \\
n &= 3; & r_3 &= \frac{9h^2}{4\pi^2\mu\epsilon^2}; & w_3 &= \frac{8\pi^3\mu\epsilon^4}{27h^3}. \\
& & &= 9r_1 & &= \tfrac{1}{27}w_1
\end{aligned}$$

If we now substitute these r and w values in the energy equation, the kinetic energy of the electron upon the nth orbit will become

$$E_{1,\,n} = \tfrac{1}{2}\mu r_n^2 \cdot w_n^2 = \tfrac{1}{2}\mu\left(\frac{2\pi\epsilon^2}{nh}\right)^2.$$

The energy change involved when the electron is brought from orbit n to orbit m is expressible as

$$\Delta E = \tfrac{1}{2}\mu\left(\frac{2\pi\epsilon^2}{h}\right)^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right).$$

This energy, obviously, is either absorbed by the atom or released from it during transformation and according to the frequency relation of Bohr it is equal to $\Delta E = h \cdot \nu$, where ν designates the frequency ($v = c/\lambda$) emitted during the change from the higher to the lower energy state.

We may write, accordingly, that

$$\begin{aligned}
\nu = \frac{\Delta E}{h} &= \frac{1}{2} \cdot \frac{\mu}{h}\left(\frac{2\pi\epsilon^2}{h}\right)^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \\
&= R\left(\frac{1}{n^2} - \frac{1}{m^2}\right).
\end{aligned}$$

Since both n and m are postulated as whole numbers only, this last expression is identical to the series formula arrived at by Balmer from purely empirical considerations of the lines in the hydrogen spectrum. We recognize and identify here the constant N appearing in the series formula as the universal constant R, the so-called Rydberg constant, universal because it involves only universal atomistic constants, whose values had been previously determined. R is determinable from the above equation, viz.:

$$R = \frac{2\pi^2\epsilon^4\mu}{h^3}.$$

This numerical magnitude of R has been derived from the frequency relationship of Bohr. In a previous section we derived the formula $N\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$ for the wave numbers of the emitted frequencies. Numerically, therefore, N and R must be mutually related according to the expression $N = R/c$, where c is the velocity of light.

From the accepted values of $\mu = 9 \times 10^{-28}$, $\epsilon = 4.77 \times 10^{-10}$, $h = 6.53 \times 10^{-27}$, and $c = 3 \times 10^{10}$, we calculate $N = 109{,}678$, which is in remarkable agreement with the magnitude as empirically obtained above by Balmer. The establishment of this equivalence constitutes the fundamental achievement of Bohr's theory and is a strong support of it.

Moreover, a second confirmation, of great importance, follows directly from this. For a long time a spectrum was known to observers in astrophysics which could never be reproduced in the laboratory. This series was discovered by Pickering in the spectrum of the star ζ Puppis and was attributed by him to the presence of hydrogen. The lines of this spectrum were expressible by an analogous Balmer formula,

$$\nu = N\left(\frac{1}{2^2} - \frac{1}{p^2}\right), \qquad p = 2.5, 3.5, \cdots.$$

Bohr's theory demanded that this new series does not belong to hydrogen but rather to helium and indeed to helium with a single positive charge. This latter may be described as a system mechanically similar to hydrogen, i.e., it is composed of a nucleus with one rotating electron, but differing from it electrically because the electron rotates about a nucleus with a double positive charge, whereas in hydrogen the nucleus has but one charge (proton). Consequently, the Coulomb attractive force for this system is $C = 2\epsilon \cdot \epsilon / r^2$, and not $\epsilon \cdot \epsilon / r^2$ as in the case of hydrogen. In the derivation of Rydberg's constant for such a system all magnitudes remain unaltered except the coefficient 4, due to the occurrence of the factor $(2\epsilon^2)^2$ instead of the term $(\epsilon^2)^2$, i.e., $= 4\epsilon^4$. R for helium with a single positive charge is, therefore,

$$R_{\mathrm{He}} = \frac{2\pi^2 \cdot 4\epsilon^4 \cdot \mu}{h^3} = 4\left(\frac{2\pi^2\epsilon^4\mu}{h^3}\right) = 4R_{\mathrm{H}}.$$

F. Paschen subsequently demonstrated that the Pickering series is due to helium and proper to helium atoms with a single positive charge. The Pickering series may thus be represented by the Pickering-Balmer formula,

$$\nu = 4R_{\mathrm{H}}\left(\frac{1}{4^2} - \frac{1}{p^2}\right), \qquad p = 5, 6, \cdots.$$

We must refrain from delving further into the details of the theory. We may mention, however, that the theoretical development of Bohr's conception of the hydrogen spectrum by Sommerfeld and the experimental investigation of the spectrum of helium by F. Paschen have afforded a deeper insight into the structure of these simple atoms and they have demonstrated that the simple calculation, as indicated above, is merely a first approximation of the true values; furthermore, they indicate that the nucleus itself is not stationary but that its mass also is in motion on account of which the Rydberg constant for H and He cannot be exactly alike.

On the other hand, we may deduce, from the fact that the line spectra of other elements are classifiable similarly in series, that the emission processes taking place in these elements proceed essentially as in the case of hydrogen and that the structures of these atoms are closely analogous to that of hydrogen. On the principles of Bohr's theory, the deviations of the series formulæ of other elements from those of hydrogen suggest to us the typical properties of these elements. In addition, the series of the Roentgen spectra also present similar regularities; they reveal the internal structure of the elements.

Graphic Representation of Hydrogen Spectrum

In recapitulation, we will again remark that a spectral line arises when an atom reverts from a condition of higher energy to one of lower energy, the liberated energy ΔE (= energy difference of the two states) being emitted as a monochromatic radiation of frequency ν, so that according to Bohr's frequency relation

$$\nu = \frac{\Delta E}{h} \cdot$$

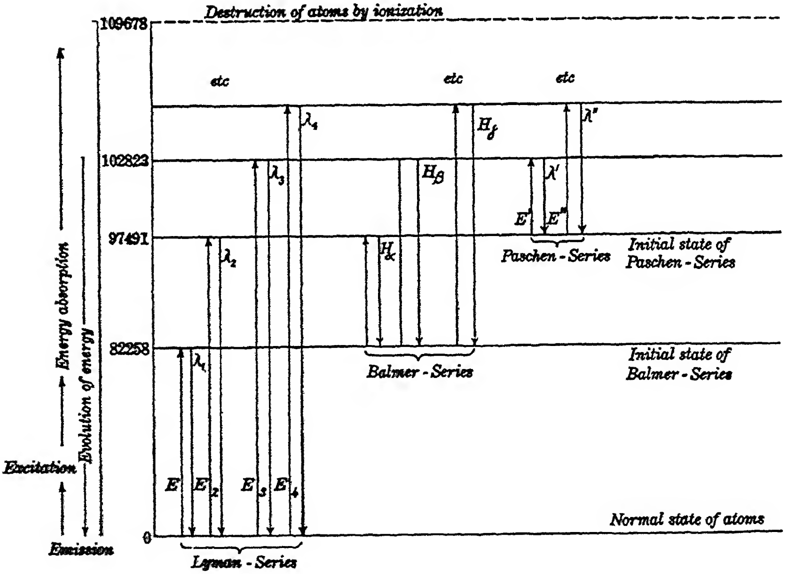

FIG. 36.

Since h is a constant, the differences in the energy levels of the respective states may be expressed in a relative measure in terms of the frequencies ν (or the wave numbers $n = 1/\lambda = \nu/c$). We thus have the following figure (Fig. 36). The Lyman series will arise from the normal atomic state,

$$\nu = N\left(\frac{1}{1^2} - \frac{1}{p^2}\right), \qquad p = 2, 3, 4, \cdots.$$

The numbers placed along the left edge of the diagram designate the wave numbers which are proportional to the energy differences of the several atomic states and likewise are the reciprocal values of the wave-lengths λ_1, λ_2, etc., $N\ 1/1^2$ is the initial, or normal, state, i.e., the "basic term," while $N\ 1/2^2$, $N\ 1/3^2$, $N\ 1/4^2$, etc., represent the "higher" states, the "excited terms."

Balmer's series

$$\nu = N\left(\frac{1}{2^2} - \frac{1}{m^2}\right), \qquad m = 3, 4, 5, \cdots,$$

shows us directly that the initial state of this series is that in which the atom exists after excitation of the first Lyman line, namely, the line $N\ 1/2^2$, while the terms $N\ 1/m^2$ correspond to the other end terms of the Lyman series. But whereas in the Lyman series the excited terms $N\ 1/p^2$ combine with the fundamental term $N\ 1/1^2$, the Balmer series arises through the combination of the terms $N\ 1/3^2$, $N\ 1/4^2$, etc., with the term $N\ 1/2^2$.

Similarly, $N\ 1/3^2$, the fundamental term of the Paschen series, is also the end term of the second Lyman line or the end term of the first Balmer line, while the higher members of the Paschen series arise during the transition of the atom from the higher states $N\ 1/4^2$, $N\ 1/5^2$, etc., into the lower energy state $N\ 1/3^2$.

In this wise is explained the origin of the simplest spectrum according to the physical interpretation of the Combination Theory of Ritz.

The more complex atoms have more excited states than the hydrogen atom, i.e., more combination schemes are possible and consequently there are more spectral lines. The principles of modern spectroscopy, however, give us a fair exposition of the hydrogen spectrum.

CHAPTER XIII

THE CONDITIONS FOR EXCITATION OF THE ROENTGEN SPECTRUM

We shall continue to discuss, in this chapter, the methods whereby optical spectra may be produced through the agency of electronic impacts. We shall note, particularly, the several phenomena arising as the electronic velocity is gradually augmented; furthermore, we shall so modify the experimental conditions that the impacting electron will impinge upon solid bodies rather than upon gaseous or vapor atoms or molecules. Experiment has demonstrated conclusively that bodies impacted by high velocity electrons become "electronic radiators," i.e., they themselves eject secondary electrons; in conjunction with the ejection of these "secondary electrons" a simultaneous electro-magnetic radiation is emitted by the solid, which is termed Roentgen radiation or X-radiation.

A few remarks may be expressed concerning the general problem of the character of Roentgen rays. The true nature of X-radiation is known definitely today. Precise and critical experimentation has shown that Roentgen radiation is a wave phenomenon, an electro-magnetic pulsation essentially analogous in character to other electro-magnetic radiation, differing therefrom only in their respective wave-lengths. The discovery of X-ray interference phenomena by Laue, Friedrich and Knipping and the subsequent proposal of an optical theory to explain these phenomena accentuate and amply confirm this similarity. The more recent researches of Moseley, W. H. and W. L. Bragg, E. Wagner, Debye, Scherrer, et al., offer conclusive evidences to corroborate and substantiate this view. On the other hand, experiments carried out prior to the conclusive work cited above presaged the ultimate explanation of this problem. Although the experimental efforts of E. Marx[1] to determine the velocity of this radiation did not yield effective and thoroughly convincing data in every respect, the observed polarization phenomena suggested the transverse vibrational character of the radiation. It may be mentioned, in passing, that Ketteler proposed an hypothesis, shortly after the discovery of Roentgen rays, stressing their transverse vibrational nature as opposed to the explanation, then prevalent, which regarded them as "longitudinal ether waves."

We will now consider briefly some other methods to demonstrate the undulatory nature of Roentgen rays and the measurement of their wave-lengths.

The problem of X-ray emission was attacked from our modern theoretical point of view as early as 1906 by M. Wien, when he proposed to compute their wave-lengths on the basis of Einstein's "photoquantum" hypothesis. Essentially, this follows the same trend of thought that inspired the successful experiments of Franck and Hertz in the optical regions and which culminated in the "excitation theories" described in the previous chapter. From the excitation energy ϵV of the electron and the quantum relation $\nu = \epsilon V/h$, Wien computed the frequency of the X-radiation, arriving at wave-lengths of the order 1 – 0.1 Å.

About the same time, B. Walter, Pohl, Haga and Wind commenced their researches to establish evidence of the diffraction of Roentgen rays at very narrow slits. These investigations, however, did not establish convincing evidence of this phenomenon even though the probability of its existence had been accentuated because of the photometric re-evaluation (1912) of the photographic images of the slits by P. Koch and the calculations based upon them by Sommerfeld. Only in recent years, after years of continued and uninterrupted efforts, has B. Walter succeeded in demonstrating very definitely the diffraction of X-rays at wedge-shaped slits and in calculating the wave-lengths of the X-rays utilized by

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[1] The reader is referred to discussion on Roentgen rays, by E. Marx in "Handbuch der Radiologie," Vol. 5.

measuring the distance of the diffraction image to the direct image and evaluating according to the method of computing optical wave-lengths. The X-rays originating from a copper anticathode were made to pass through a wedge-shaped slit at a distance of 75 cm. from the discharge tube, the slit being adjustable to a length of 18 mm. and a maximum width of 14 μ. A photographic plate was placed 75 cm. behind the slit. Diffraction images of the slit were produced on both sides of the direct image so situated that their distance from the direct image agreed closely with the anticipated value on the simple theory of the diffraction of waves at narrow slits. From a series of measurements obtained by taking the distance of the diffracted images at various places (order of magnitude 100 μ) to their proper slit widths (order of magnitude 2–4 μ) the wave-length of the radiations emitted by the copper was found to be 1.38 to 1.68×10^{-8}, which is in thorough agreement with other values obtained according to the more exact crystal diffraction method which will be described later (1.54×10^{-8} cm.).

While the search for this fundamental diffraction phenomenon was in progress culminating in its eventual observation and evaluation after ceaseless efforts extending over a period of 20 years, Larson, Siegbahn and Waller experimentally demonstrated at Lund the ordinary refraction of X-ray taking place in a prism, for which Roentgen had searched in vain and whose non-appearance under normal optical conditions led Ketteler to the assumption that Roentgen radiation is characterized by very small wave-lengths. It is immediately apparent that the experimental procedure to demonstrate this phenomenon must be different intrinsically from that utilized in the prismatic dispersion of an ordinary optical spectrum. In this instance the incidence angle must be taken as small as possible. The experimental arrangement showing the observed refractions and reflections is depicted in the following diagram 37.

The observed refraction makes possible the determination of the index of refraction of the prism substance for X-radiation of various wave-lengths, i.e., we may determine the dispersion produced by crystalline and amorphous bodies for very small wave-lengths. The data for a number of such preliminary experiments are given below. The density of the glass prism was 2.551 and the index of refraction for visible light of about 5,000 Å. was about 1.6.

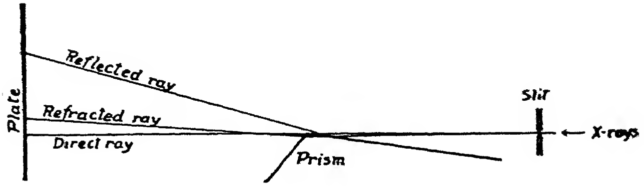

Fig. 37.

Wave-lengths in Å. U.	Index of Refraction
1.993	$1.0000123_8 \pm 0.4 \times 10^{-6}$
1.750	$1.0000100_8 \pm 0.4 \times 10^{-6}$
1.538	$1.00000812_5 \pm 0.05 \times 10^{-6}$
1.389	$1.00000664_8 \pm 0.05 \times 10^{-6}$
0.708	$1.00000164 \pm 0.01 \times 10^{-6}$
0.630	$1.00000122 \pm 0.15 \times 10^{-6}$

The wave-character of Roentgen radiation is thus established by two normal optical methods: the (bi-mensional) diffraction at a slit and the prismatic refraction and spectral dispersion. The third method, which alone is serviceable to exact wave-length measurements, is based upon the interference of Roentgen rays taking place at three dimensional crystal gratings, the phenomenon discovered by Laue, Friedrich and Knipping. This method of measuring absolute wave-lengths of X-rays by means of interference phenomena produced at the space lattice of crystals is closely analogous to the ordinary optical method to determine the wave-lengths of visible light, by means of the diffraction produced in line gratings. For the moment, we will consider only the principle upon which this lattice method is based. The observations made by Bravais, Groth, and Schoenfliess indicate unmistakably that the ultimate constituents of crystals, their so-called "structural bricks," are grouped in a definitely regulated arrangement known as their space lattices. The relative spacing between these "bricks" is readily computable if the system to which the crystal belongs is known; that is, if the type of space lattice characteristic of the crystal is known. Let us consider the crystal form of sodium chloride. This substance crystallizes in the cubic system, the individual crystals being so constructed that each sodium ion is surrounded at equal distances by six chlorine ions, and each chlorine ion, in turn, by six symmetrically spaced sodium ions. The distance between two dissimilar ions is termed the grating constant "d" of the crystal; the distance a ($= 2d$) between two like ions represents the edge of the elementary cube of the cubic lattice. Suppose a cube of edge d to be circumscribed about each ion. Obviously, a rock salt crystal will be comprised of a number of such mutually contiguous cubes, its natural structural units. Two adjacent cubes will thus contain one atom of A_1 and one of A_2 in a total volume of $2d^3$. The density of a given crystal mass is expressible by $\sigma = \frac{\text{mass of atom}}{\text{volume of cube}}$. If N designates Avogadro's Number (6.06×10^{23}), the mass of a given atom is equal to the atomic weight divided by N. Or the density equation may be written as

$$\sigma = \frac{A_1 + A_2}{N} \cdot \frac{1}{2d^3}.$$

From this equation the absolute value of the spacing between the two atoms, i.e., the grating constant, is easily determinable; viz.:

$$d = \sqrt[3]{\frac{A_1 + A_2}{2} \cdot \frac{1}{\sigma} \cdot \frac{1}{N}}.$$

For crystals of sodium chloride, we have the following data:

$$A_{\text{Na}} = 23.00,$$
$$A_{\text{Cl}} = 35.46,$$
$$\sigma = 2.164,$$
$$N = 6.06 \times 10^{23},$$
$$d = 2.814 \times 10^{-8}.$$

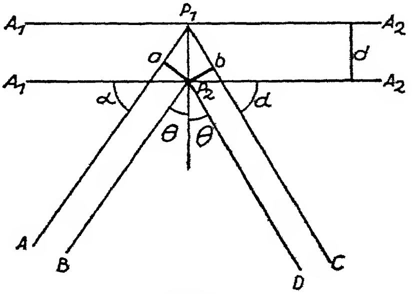

FIG. 38.

In Figure 38, A_1A_2, A_1A_2 represent two planes parallel to the crystal face, each plane containing, therefore, alternate A_1 and A_2 atoms. The spacing between them is d. An X-ray beam, AB, of wave-length — for simplicity's sake this is assumed to be parallel[2]—is incident upon these planes. As is conventional in optics the angle made by the advancing ray and a normal to the points of incidence P_1 and P_2 is termed the incidence angle and designated by θ; the angle made by the ray with the plane is termed the "glancing angle" and equals $\alpha = 90 - \theta$. The exterior or limiting rays A and B of the beam will be reflected respectively from P_1 and P_2 to C and D. Due to the difference in their respective paths, the rays, though originally in phase, may not proceed in phase after reflection from the planes. The reflected rays may, therefore, cause almost complete interference, reinforcing one another only if the difference in their paths is equal numerically to their wave-length or some whole multiple of it. The difference in their paths is equal evidently to $P_1a + P_1b$. From the right triangles P_2aP_1 and P_2bP_1, this may be evaluated as $2d \cos \theta$ and also $2d \sin \alpha$. Maxima in reflection will occur thus for the specific incidence angle θ when the difference in lengths of the two paths is equal to a whole number of wave-lengths, or if

$$n\lambda = 2d \sin \alpha = 2d \cos \theta,$$

or specifically

$$2\lambda = 2d \sin \alpha = 2d \cos \theta,$$

n or 2 is the order number of the spectrum—as in optics—for

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[2] Due to their short wave-lengths, Roentgen rays cannot be rendered parallel, as are optical rays, by means of lenses or mirrors. Roentgen rays that may be regarded practically parallel can be produced by successive passage through a series of consecutive slits. The angle becomes smaller, at the expense of the ray's intensity.

several orders of reflection spectra are observable in X-ray spectroscopy as in optics.

Proceeding along these lines, it was shown that continuous X-ray spectra likewise may be produced. This phase will receive fuller discussion in the following chapter. Subsequently it was demonstrated that the characteristic radiation of an element consisted essentially of a line spectrum.

X-rays emitted by solid bodies as a consequence of electronic bombardment are of two types. A "characteristic spectrum," depending solely upon the element of the anticathode, invariably is superposed upon a continuous spectrum. While the "hardness," i.e., the intermediate wave-lengths of both emission types, is a function of the potential V, so related that the "hardness" of the radiation depends only—in conformity to the postulates of the quantum theory—upon the velocity of the "exciting" electrons and not upon their number (i.e., the current strength in the X-ray tube), the excitation of the "characteristic" spectrum arises only for a requisite minimal electronic energy whose magnitude increases with the atomic number of the anticathodic element. Expressed otherwise, the wave-length of the characteristic radiation of an element used as anticathode is the smaller (i.e., the harder) the higher its atomic number.

The "characteristic" line spectrum of an element in the Roentgen ray region differs essentially from the optical line spectra. An X-ray series consists of a group of spectral lines. Each element emits several such series which are widely separated from one another in the spectrum. To "excite" an element to the emission of any one series it is necessary to apply a specified minimal potential. In conjunction with this emission other series of greater wave-lengths are observed.

On the other hand, series of smaller wave-lengths do not appear. These latter are produced only as characteristic frequencies upon the application of still higher potentials. Whereas, in optics, each line has its own "excitation" potential, in the X-ray region this obtains only for a series, or group, or for all series of large wave-lengths. Comparison of the spectra produced by the various elements revealed a surprisingly simple relationship: the line spectra of all elements are alike structurally and superposed upon a continuous spectrum. Further, the squares of the frequencies of the several groups, which are easily recognizable by the number and the relative position of their lines, are proportional within rather wide limits to the atomic numbers of the respective elements. The individual line groups, so determined, are designated the K-series, L-series and the M-series, being arranged according to their increasing wave-lengths and decreasing frequencies (or hardness). According to this relationship (known as Moseley's law),

$$\nu_k = C_1\sqrt{Z}; \qquad \nu_L = C_2\sqrt{Z},$$

where Z is the atomic number of the element in question and C is a constant.

Mindful of these basic principles, we will now consider more thoroughly the excitation energies with reference to the continuous spectrum. (See also Chapter XIV.)

On the principles of the quantum theory, as outlined in the previous chapter, we would anticipate the emission of a monochromatic radiation of frequency $\nu = \epsilon V/h$ as a result of the energy loss ϵV by an electron subsequent to its impact with an atom. This expectation, however, is not fully realized as is indicated rather definitely by the appearance of a continuous spectrum arising from the anticathodic element even though this be bombarded with electrons of uniform velocity. The researches of Broglie, Wagner, et al., establish this fact beyond doubt. But a peculiarly interesting feature is observed in such continuous spectra. They possess sharply pronounced regions of minimum wave-lengths whose position depends upon the applied potential-difference V. In other words, the region of minimum wave-length approaches the shorter wave-lengths (i.e., higher frequencies) as the excitation energy ϵV is increased. This observation harmonizes fully with the tenets of the quantum theory according to which the energy quantum $h\nu$ of the excited radiation can be the greater, the greater the excitation energy ϵV. Of especial interest is the observation that there is an abrupt cessation in emission at a fixed wave-length. Furthermore, this limiting minimum wave-length $\lambda_{\text{min.}}$ was found to be inversely proportional to the excitation energy of the electron and entirely independent of the chemical nature of the element serving as the anticathode. The former relationship may be formulated according to the displacement law of Blake-Duane, as

$$V \cdot \lambda_{\text{min.}} = \text{constant} = 12{,}300,$$

in which the potential is measured in volts and the wave-length in Å. units. In the terminology of the quantum theory this may be written

$$V \cdot \lambda = h \cdot c / \epsilon,$$

a restatement of the more general form $\epsilon V = h\nu$. (In other words, a linear relationship exists between the kinetic energy of moving electrons and the minimum wave-length of the resultant X-radiation.) From the known values of the factor V and of the velocity of light c and of the accepted values of the elemental quantum ϵ, Planck's proportionality constant h is easily computable. The validity of this expression has been tested by several investigators. The precision measurements of E. Wagner, Blake, Duane, and coworkers yield values of h between 6.53 and 6.56×10^{-27} erg sec. To convert the constant 12,300 into absolute units it must be multiplied by 10^{-8} (the conversion factor of Å. to centimeters), and by $1/3 \cdot 10^{-2}$ to convert volts to static units. That is,

$$h = \frac{V \cdot \lambda \cdot \epsilon}{c} = \frac{12{,}300 \times 10^{-8} \times 4.77 \times 10^{-10}}{3 \times 10^{2} \times 3 \times 10^{10}} = 6.52 \times 10^{-27}.$$

The quantum law thus presents itself in a new form which shows perfect analogy to the quantum expression for the photoelectric effect. We observe here a continuous series of electronic velocities which are emitted as the result of the monochromatic frequency ν; but this continuous "velocity spectrum" extends only to a definite upper limit, the maximum electronic velocity $V_{\text{max.}}$ being given by the quantum equation

$$V_{\text{max.}} = h\nu/\epsilon.$$

We will now center our attention upon the excitation of the characteristic line radiation. We have noted above that the wave-lengths corresponding to definite line groups —characteristic for each element—make their appearance only upon application of a specified potential, several lines of such a group arising simultaneously. A "pure" or "simple" quantum result obviously does not obtain. If, however, the excitation potential $V_{\text{crit.}}$ is substituted in the relation $\nu = \frac{\epsilon \cdot V_{\text{crit.}}}{h}$, the calculated frequency of the emitted lines will be found a trifle higher than that of the shortest wave-length of the experimental emission group. This phenomenon, per se, is not readily intelligible, nor does it seem to contribute to the eventual solution of the "emission process"; but it attains both these conditions in a high degree when combined with another result.

We have had occasion previously, in the case of optical excitation, to refer to the significance of the absorption spectra of atomic gases and vapors as a possible aid in explaining the mechanism of emission processes. If we extend this method to the solution of the X-ray series, it will be noted that the monochromatic frequencies of a specific element are not absorbed selectively by this same element. This indicates that neither the initial orbits of the electron nor its final orbits are accessible without electronic excitation (i.e., without electronic impact). The initial orbit may be designated as the state of lower energy content. The assumption that the initial orbit results only from electronic impact, and therefore is not present in the normal element, is not acceptable on energy grounds. It was shown above that the energy $\epsilon V_{\text{crit.}}$ necessary for a series excitation differs but very little from the emission quantum $h\nu$. If this small energy difference suffices for the establishment of the initial orbit, it would follow, from Maxwell's distribution law, that an appreciable number of the atoms are present in this initial state. It appears reasonable, therefore, to assume the presence of atoms in the initial state. It may still be possible, however, that the final state of the atom may not be realizable by radiation absorption as well as by electronic impact. According to the mode of expression previously adopted—in Chapter XI—this conjecture may be formulated somewhat as follows: the electron cannot be transposed directly from its initial orbit to a final orbit either by the absorption of radiation or through the medium of electronic impact. In other words, the energy corresponding to the difference in energy content of the two states—which would be equal to the quantum of emission $h\nu$—is not absorbable.

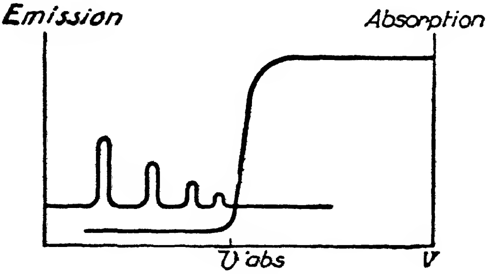

FIG. 39.

On the other hand, a more critical survey of absorption phenomena indicates definitely the strong absorbability of frequencies which are but a trifle greater than the shortest waved emission frequency of a given series. (See Fig. 39.) If the equivalent electron energy is computed from the quantum relationship by means of this absorption frequency $\nu_{\text{abs.}}$ (which constitutes the beginning of an absorption band of which $\nu_{\text{abs.}}$ itself is the maximum frequency), it will be observed that $\nu_{\text{abs.}}/V_{\text{crit.}} = \epsilon/h$; that is, the quantum relationship is rigidly valid for this specific frequency. A pronounced ionization simultaneously takes place, the electron being displaced from its normal orbit within the atom to an exterior position; i.e., the electron becomes "free." Exactly the same sequence of phenomena was observed, it will be recalled, at the end of an optical series.

The problem thus becomes more lucid and clear. An electron cannot be withdrawn directly from its initial orbit as a consequence of absorption or electronic impact and become localized in those final orbits from which it may revert, in turn, to the initial orbit with a concomitant emission of a monochromatic series. This higher energy level whose establishment is prerequisite to rendering the atom capable of emitting Roentgen lines corresponds to its ionization.

On this experimental basis, W. Kossel recently constructed a scheme of Roentgen ray emissions to which we shall adhere with but slight modification. Before entering into a discussion of this, we may cite one more experimental observation. Our knowledge of the absorption spectrum that invariably accompanies each series has been extended rather appreciably by the refinement in the technic of X-ray spectroscopy developed by Siegbahn and his students. Whereas reference was made formerly to "sharp absorption band boundaries," Stensson et al. have demonstrated that the absorption actually is characterized by a "fine-structure," comprised of individual and discrete absorption lines which merge into a continuous band. Furthermore, it was noted that the complete K-series was emitted when a critical potential was exceeded, and that the L, M, N, etc., series consisted of subgroups, each of which has its own characteristic excitation potential whose magnitudes, to be sure, lie close together.

The theory of atomic structure as postulated by Kossel is somewhat as follows. Each element has disposed about its nucleus a number of electrons equal to its atomic number. Whereas the optical series result from the excitation of the exterior electrons, the energy changes incidental to the production of X-rays are attributable to the excitation of "inner electron groups." The more closely situated an electron to the nucleus, the greater will be the energy requisite for its transfer from its normal to a more distant orbit. These electrons are distributed in equally quantized groups, each group corresponding to a definite energy state difference with respect to infinity. These respective energies must be applied to withdraw an electron from its normal group; they constitute the energy-steps, or excitation-steps, of the series. Many of the groups are distinguishable from one another only by very small differences in their energy contents. The excitation potentials of the line subgroups of the L, M, etc., series correspond to these. An exchange of electrons does not take place between groups of equally quantized electrons; furthermore, each group is so complete within itself that transfer of an electron from one to another cannot take place even if the energy necessary thereto, as computed from the differential energy contents of the respective groups, be imparted to it. On the other hand, if a given group has become deficient through the complete removal of an inner electron from the atom, transference of electrons within the inner groups may take place with the simultaneous disengagement of energy. Theory in this wise conforms with the experimental observations. Regeneration of the inner groups takes place with energy evolution in the form of monochromatic radiation—the X-ray series. To produce the K-series work must be done in order to remove an electron from the innermost group—the K-group of the atom—the K-series having the largest emission quantum, the largest frequency of the atom. The deficiency in number of electrons thus arising in the K-group is compensated for by the transfer to it of an electron from the L- or M-group. The shortage in electrons is thus carried over into the group that yielded the compensating electron, which is replenished, in turn, in a somewhat similar manner by the transfer to it of electrons from such groups situated at still greater distances from the nucleus. Thus, the emission of the K-series (i.e., regeneration of the deficiency in the K-group) is inevitably accompanied by the simultaneous emission of all series of longer wave-lengths. The "Principle of Correspondence" proposed by Bohr offers a rather plausible explanation why the "regeneration" of a given group should be accomplished by electrons of adjacent rather than of more distantly situated groups. On this explanation, not only the position of the several lines in the spectra, but their relative intensities as well, are in qualitative agreement with the experimentally observed data.

To excite n atoms of an anticathode to K-radiation, energy to the extent of $n \cdot \epsilon \cdot V_{\text{crit. K}}$ will be required. A number of these atoms, say m, will emit the "regeneration" radiation of the immediately adjacent group. This gives rise to the K_α line. Simultaneously, n atoms ($n < m$) will regenerate themselves from the adjacent exterior group of electrons giving rise to the K_β lines of shorter wave-length, i.e., of greater frequency than the K_α lines corresponding to the greater energy difference of two groups. This exchange of electrons from one shell to another will continue to the outermost group, to the so-called "optical electrons." An energy difference still exists, however, between the outermost electrons and "infinity," although this is small in comparison to the energy differences between the K-group and the successive exterior electrons. The "optical orbits" normally unoccupied lie in this region. Evidently, what has been said thus far relative to the transposition of electrons from one occupied orbit to another does not apply in this region. Furthermore, there is no obvious reason why an electron could not be removed from its normal orbit, say from the K-group, to an "optical orbit." The "fine structure" of the absorption bands is explainable on this basis; thus, this may be attributed to the discrete optical orbits to which an electron normally localized within an inner orbit may be withdrawn by the absorption of radiation. Since the corresponding regeneration radiations are lacking in these emissions, it is too highly improbable that an electron will return directly to its initial orbit from an optical orbit.

Our observations and study of the excitation of X-rays and related phenomena have evoked, quite involuntarily, certain conclusions concerning the structure of atoms. To recapitulate: the similarity in the spectral series of all the elements suggests unmistakably a similarity in the internal structure of the electronic shells of all elements. Then, too, certain specific properties recurring at regular intervals for the various elements suggest the distribution or localization of the electrons in groups of equal energy. Finally, the coincidence of the boundary of the emission series and the beginning of the absorption series indicates the similarity and correlation of the optical and X-ray emissions. Bohr has formulated certain principles whereby the respective emissions of the various atoms makes possible a "visualization" of the "regularities" of atomic structure. For, the same electron orbits, which constitute the "exterior" electronic orbits in the case of elements of low atomic number, that is, the shells of the optical and also the chemical electrons, become inner orbits for higher atoms and, by analogy, their electrons become X-ray electrons.

Atoms of low atomic number possess fewer electrons and, therefore, fewer electron-groups than the heavier elements. It may be anticipated, accordingly, that the complete X-ray spectra due to electrons of elements occupying various positions in the periodic system will be differentiated one from another in that the spectra of lower elements contain fewer line groups than those of heavier elements. Even more: we may reasonably expect that X-ray series may become "optical" series.

The electronic shell of helium is comprised solely of two electrons and these are "exterior" electrons and therefore optical electrons also. This group persists as such in all the other elements and constitutes in them the so-called K-group. In addition to this K-group, the elements following helium possess one or more additional electrons further removed from the nucleus than are the electrons of the K shell. In these "optical" electrons are developed the Roentgen ray L-group emissions of the heavier elements. As long as this second group remains incomplete the element cannot possibly emit L-radiation, the emission containing only K-radiation. We may express this differently by saying that the L-radiation of these elements coincides with their optical line emissions. The successive or "step-wise" appearance of the K, L, M, etc., series is fully in accord with this observation.

The increase in the required excitation energy and the accompanying increase in frequency of the emitted series, noted for elements with increasing atomic numbers, follows from the progressively increased attractive force between nucleus and electron inasmuch as the positive charge of the nucleus becomes larger. Even though the electronic groups, or shells, are thereby tractated closer to the nucleus, their relative configuration and their absorption capacity for the excitation energy remain the same. These notions epitomize the reliable and trustworthy conclusions that may be drawn from the experimentally determined habitus of the X-ray emissions. (See Chap. XV.)

CHAPTER XIV

The Continuous X-Ray Spectrum

During the course of his investigations on the secondary X-rays emitted when X-rays are made to impinge on a substance, Barkla was the first to find this radiation to consist of two parts, of which only one was characteristic of the substance of the secondary radiator. The other, on the other hand, proved entirely independent of the nature of the substance and exhibited a behavior almost entirely similar to that of the primary radiation. Polarization phenomena arising with this secondary radiation decidedly favored the conception that X-rays are transverse vibrations and paved the way to a correct understanding of the primary emission originating in the anticathode. From the electron theories in vogue at the time, the mechanism of X-ray production may be conceived somewhat as follows. The cathode ray electrons impacting against the anticathode are stopped by it and radiate, in conformity to the laws of classical electrodynamics, a continuous spectrum whose wave-lengths and "intensity distribution" are determined by the duration of stoppage and the velocity of the cathode rays. This spectrum is called "bremspectrum" because of the manner of its production in contrast to the characteristic line spectrum (Chapter XIII) which owes its formation—speaking very generally—to certain definite conditions in the atoms of the anticathode material, i.e., the secondary radiator.

This conception and its mathematical formulation sufficed in general to explain the data acquired with the methods available at the time on the polarization of radiation, the increase of "hardness" with voltage applied to the X-ray tube as well as the intensity distribution and the dependence of "hardness" on the azimuth of observation direction with respect to the direction of the cathode rays.[1]

The discovery, by Laue in 1913, of the interference phenomena of X-rays at crystal gratings and the subsequent elaboration of practical methods by Bragg and de Broglie greatly enhanced this sphere of physical research by making possible quantitative spectral analysis in the region of high frequency electro-magnetic vibrations. The characteristic radiation appeared as a pure line spectrum while the "brems-radiation" proved to be a continuous spectrum. The latter will receive detailed consideration in the following pages.[2]

The intensity variation ($J_\lambda = f(\lambda)$) of the continuous spectrum (Diagram 40) shows a surprising similarity to the corresponding curve for thermal radiation; and yet there are marked differences. While the intensity curve of the thermal spectrum approaches the abscissæ axis asymptotically for both small and large wave-lengths, the intensity curve of the continuous X-ray spectrum does not approach zero for short wave-lengths, but stops abruptly, cutting the axis at definite short wave-lengths. This fact questioned the validity of classical electrodynamics and necessitated thorough and fundamental experimental study of this spectrum to establish a criterion for the tenableness of theoretical speculations regarding the genetic mechanism of continuous Roentgen spectra.

Attention was next focussed upon the investigation of those portions of the spectrum where the intensity curve falls off sharply to zero, i.e., to the short waved (high frequency) end of the spectrum. These points correspond, obviously, to definite wave-lengths $\lambda_{min.}$ or frequency $\nu_{max.}$. Duane and Hunt[3] summarized the results of their researches on the factors that determine this end of the spectrum (Duane-Hunt law) as follows: the wave-length of the

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[1] For details, see the article by R. Pohl in the "Physik der Roentgenstrahlen"; Marx, Handbuch der Radiologie, Vol. 5; and P. Cermak, "Roentgen Rays."

[2] E. Wagner, Report on the Continuous Roentgen Spectrum, Jahrb. d. Rad. u. El. 16 (1920).

[3] Duane and Hunt, Phys. Rev. 6, 166 (1915).

high frequency end of the spectrum is so related to the potential applied to the X-ray tube that the product of the wave-length and the voltage is constant. This may be expressed as

$$\lambda_{\text{min.}} \cdot V = k; \quad \nu_{\text{max.}} = k' \cdot V;$$

where

$$\nu = c/\lambda \text{ (}k\text{ and }k'\text{ are constants).}$$

This law may be restated: for the emission of a definite wave-length a certain minimal voltage is necessary, or $V_{\text{min.}}\lambda = k$.

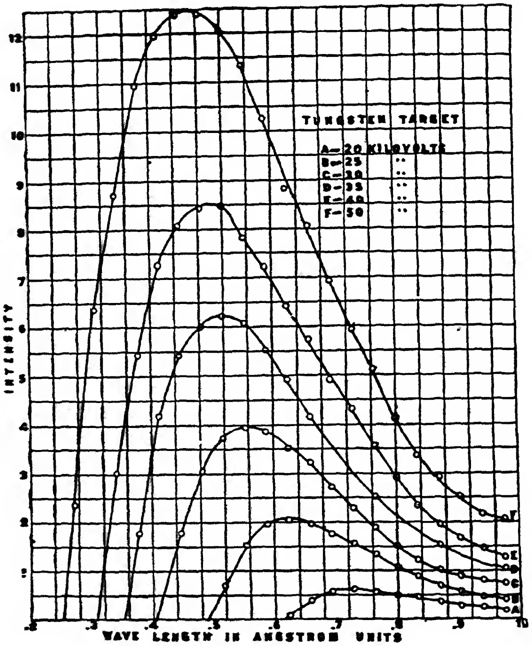

FIG. 40.

The Duane-Hunt law may be deduced from experiment in both these forms according as one has observed "isochromatics" or "isopotentials." Isochromatic curves represent for the one and the same wave-length the dependence of the intensity on the applied excitation potential. Isopotential curves, on the other hand, indicate the variation in intensity, i.e., the distribution of energy, among the wave-lengths of the spectrum for a constant excitation potential.

Figure 40 shows several isopotential curves, i.e., the spectra obtained for increasing potentials. Figure 41 depicts three isochromatic curves. In the former it will be observed that the intensity is low for the longer wave-lengths and increases to a maximum with decreasing wave-lengths, dropping sharply to zero for a definite wave-length, i.e., at the short wave boundary of the spectrum; for the latter it will be observed that a well-defined wave-length arises for a given potential which is the higher the shorter the wave-length.

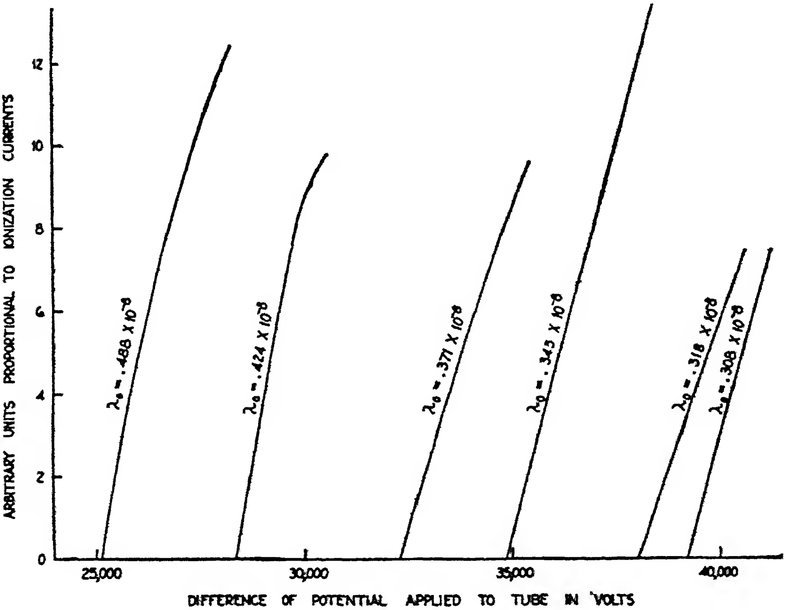

FIG. 41.

Duane-Hunt's law is of especial significance on the one hand in that it conforms quantitatively to Einstein's energy equilibrium $\epsilon V = h \cdot \nu$, thereby assigning a principal rôle in the theory of the continuous spectrum to this fundamental quantum principle. Moreover, it is in agreement with Wien's displacement law. The validity of this relationship was tested subsequently by Hull and by Hull and Rice for wider potential ranges, and recognized by Webster as independent of the anticathode material. Duane, Wagner and others[4] based upon it, with variation of all experimental conditions, a precision determination of the universal constant h, thereby so strengthening confidence in its validity that the reality of contradictory data seems incredible.[5] The constant k may be evaluated in accordance with Einstein's relation as follows:

$$\epsilon V = h \cdot \nu = h \cdot c/\lambda; \qquad \lambda V = hc/\epsilon = k;$$

putting $h = 6.52 \times 10^{-27}$ erg sec. and $\epsilon = 4.77 \times 10^{-10}$ e.s.u., k becomes $= 4.1 \times 10^{-7}$.

If λ is measured in Å. and V in volts, we obtain the useful form for general calculations $\lambda V = 12{,}340$; if V is expressed in kilovolts, as is customary in X-ray technic, this becomes $\lambda V = 12.3$. Even though the existence of these minimal wave-lengths unequivocally and definitely demonstrates the inadequacy of the classical electrodynamic theory, a second objection has been raised against this conception by Wagner in his investigations to which reference has already been made. On the assumption of a definite duration of stoppage ("bremsdauer") of the cathode ray electron a type of Doppler-Effect is to be expected which would become manifest in a dependence of wave-length upon azimuth. Tests made upon undispersed radiation seemed to substantiate this conclusion. Wagner, however, showed this to be erroneous due to the imperfections in the method used (absorption analysis) and,

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[4] Wagner, Ann. d. Phys. 57, 401 (1918). Duane, Palmer and Chi-Sun-Yeh Phys. Rev. 18, 98 (1921).

[5] The contradictory results of Lillienfeld's experiments (Jahrb. d. Rad. u. El. 16 (1920)) have been examined by Karolus. None of Lillienfeld's results and measurements were verified. On the contrary the limiting wave-length $\lambda_{\text{min.}}$ was found to be independent of all discharge conditions, and independent also of the potential corresponding to the displacement law.

furthermore, the short wave end (high frequency) of the spectrum is totally free from Doppler-Effect. Only the intermediate frequencies (and these alone are accessible to absorption analysis) revealed a dependence upon azimuth, being greatest in the direction of the cathode rays. This effect[6] is the result of the principle of the conservation of momentum; the classical Doppler-Effect does not apply.

Whereas the investigation of the short waved (high frequency) end of the continuous spectrum progressed relatively easily, the precise determination of the true energy distribution in the continuous spectrum has been encumbered for a long time by rather serious experimental obstacles which today have been for the most part surmounted. We shall not dwell in detail on the several investigative methods to which the Roentgen spectrum has been subjected and which were developed in the course of time and modified for special researches of this problem. We shall confine ourselves and outline merely the principal arrangement and method of measurement so as to understand and appreciate more fully the progress of the more recent experimental work in this field. According to the quantum laws, the electrons comprising the cathode stream in an X-ray bulb lose their energy of motion in the atomic fields of the anticathode, a few parts in a thousand of it being transformed into Roentgen radiation. This, in turn, is emitted from various depths below the surface of the anticathode depending upon the penetrating power of the electrons and consequently must permeate layers of the anticathode of greater or lesser thickness. There results, therefore, a filtered, i.e., a selectively weakened, radiation; this beam leaves through the glass walls of the tube or through an aluminum window, thereby experiencing a second filtration effect, and after passage through slits, which sharply define it, it impinges upon the spectrometer crystal, is reflected therefrom and eventually made accessible for intensity measurements. Here the dependence of the

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[6] Wagner, Phys. Zeitschr. 21, 621 (1920). March, Phys. Zeitschrift, 22, 429 (1921).

reflecting power of the crystal on wave-length exerts a disturbing influence because the intensity distribution of the individual wave-lengths can be varied with each absorption and reflection. The absorption effect experienced by the radiation in its passage through the glass of the aluminum window of the X-ray tube and the air space traversed by it between the tube and the measuring device may be calculated without great trouble by means of known absorption coefficients.

Extensive investigations are necessary to study thoroughly the absorption effects in the anticathode and the reflecting power of the spectrometer crystal. Wagner and Kulenkampff [7] have undertaken the task to determine the influence of these factors. The data of their measurements made on a calcite crystal may be summarized by the following equation:

$$R = \text{const.} \frac{\lambda(1 + \cos^2 2\varphi) \cos \varphi}{\sin 2\varphi} .$$

(φ is the glancing angle, valid for the first order and the (100) plane.)

The absorption experienced within the anticathode [8] is determinable by extrapolating the true intensity from the dependence of the observed intensity upon the angle which the rays (observation direction) make with the surface of the anticathode.

Furthermore, a precise and unquestionable method for energy measurement is essential for the correct determination of the energy distribution in the continuous spectrum of the Roentgen rays; but such a method is beset with many difficulties. However, since this problem has been solved to a considerable extent in recent times and is of significance not only scientifically but in practice as well, we shall discuss it in detail. Three general methods are available for measuring energy. Of these, the first to suggest itself is,

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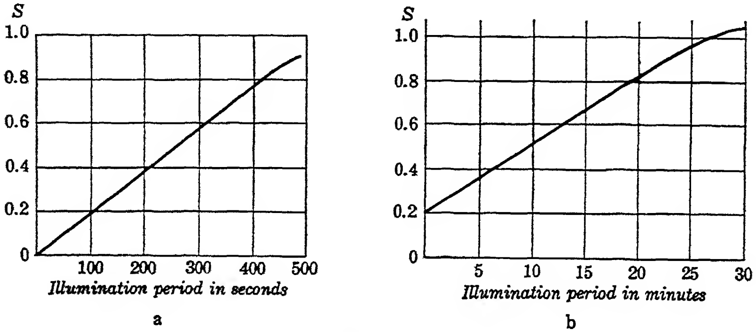
[7] Wagner and Kulenkampff, Ann. d. Phys. 68, 369 (1922).

[8] Kulenkampff, Ann. d. Phys. 69, 548 (1922).

naturally, the bolometric or thermoelectric method, which directly converts the energy of the Roentgen rays into electric, calorific or mechanical units if proper provision be made for its complete absorption in the measuring instrument. This method, however, is extremely difficult in practice and for this reason is not employed frequently in scientific investigations, particularly since it cannot be refined to sufficient sensitiveness. Nevertheless, it serves always as the basis for physical measurements. It is very valuable also because it has become possible, as the result of recent experiments, to correlate the two other methods for measuring energy, the photographic and the ionometric methods, to the absolute bolometric method.

The photographic method is based upon the darkening of photosensitive emulsions by Roentgen rays. It has been known for some time, from the work of Koch and Friedrich, that the law expressing the "darkening" of photographic plates by Roentgen rays is simpler than the corresponding law for the ordinary visible light effect. "Darkening" may be defined as follows: if the light penetrating respectively through a blackened portion of a photographic plate be compared to that transmitted by an "undarkened" portion, i.e., one previously screened from the action of light, "darkening" may be defined as the difference of the Briggs logarithms of the two observed intensities. For optical light the "law of darkness," i.e., the equation showing the dependence of the extent of darkening on the intensity J of the absorbed light and on the time t of illumination, has the following complicated form, $S = c \cdot J \cdot t^p$, p being the so-called Schwarzschild exponent. For X-rays of any wave-length this is found to be equal to 1.

Koch and Friedrich have confirmed that the darkening of the plate is a linear function of the intensity of the illumination and independent of the absolute magnitude of the illumination period. The dependence of darkening on the period of illumination has been investigated in an especially exhaustive manner by Glocker and by Bouwers, the former confining his work to small darkenings, while Bouwers also investigated larger "darkenings." For smaller darkenings (in Glocker's experiments up to about $S = 0.65$) there is a linear dependence of darkening upon the period of illumination provided definite directions are followed for the development of the plate, particularly keeping constant the temperature during development and developing for a long time. The following Figures 42*a*–42*b* represent graphically two sets of measurements for (*a*) shorter and for (*b*) longer illumination periods.



a b

FIG. 42.

For larger darkening areas Bouwers observed that S depends upon the logarithm of the time of exposure t, results being expressible by the relation $S = C \cdot \log(t/\tau + 1)$.[9] His data are shown graphically in Figure 43. Here periods of illumination are taken as abscissæ and darkening effects as ordinates. The intensities for the three curves are in proportion 1 : 2 : 4, the intensity variation being due entirely to

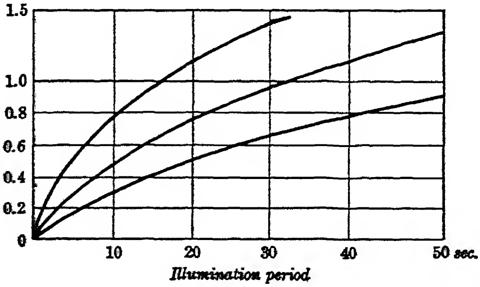


FIG. 43.

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[9] C and τ are empirically determined constants. The constant C depends primarily upon the period of development.

differences in distances. The figure demonstrates also the strict proportionality of darkening to intensity. Thus, it is evident, for example, that a darkening of 0.8 is obtained in 10 seconds for a fourfold intensity, in 2 × 10 seconds for a twofold intensity, and in 4 × 10 seconds for unit intensity. We may make the following comment regarding the formula as given by Bouwers. Whereas the Schwarzschild formula, to which previous reference has been made, is used ordinarily to express the relationship of intensity, time of illumination and darkening for visible light, Buse recently has shown the validity and applicability of the simple Bouwers formula to this radiation. Bouwers suggests that the variance of Buse's results from those of many other authors is attributable to the size of the silver bromide particles in the emulsion. In other words, blackening (darkening) depends upon the grain size of the particles; the larger the granules, the more closely do the time-darkening curves for visible light approach that of Roentgen rays, indicating a seeming relation of wave-length of the "darkening" light to the grain size which must be considered as an essential factor. Glocker has stressed above all other things that comparable investigations of the "darkening effect" are dependent upon exact directions for development of the plates. Bouwers, accordingly, studied the influence of the period of development and noted the important fact that "darkenings" are intensified proportionately to the increase in the development period. His data on the increase of "darkening" with period of development serve as a confirmation of the old relationship of Sheppard and Mees, $S_\tau = S(1 - e^{-at})$, wherein the constant a has approximately the value 0.25. It is especially significant, therefore, that the "darkening laws" are totally independent of the wave-length of the light used, as was demonstrated for the wave-length region of 0.1 to 2 Å.

The third method, which has completely displaced the photographic method in recent times, especially in practical work, is the ionometric method (often termed the iontometric method), the measurement of the ionization current in a plate condenser by the radiation absorbed in the gas space. The intrinsic error in this method is the appearance of selective secondary radiation on the walls, the metal coatings of the condenser. Such radiations will arise if the frequency of the Roentgen radiation to be measured corresponds to the absorption frequency of the atoms of the plate material. Since the absorption capacity of air for Roentgen rays is not very large, it was customary formerly to fill the ionization chamber with heavy gases (bromine or iodine compounds). The introduction of such substances, however, renders the ionometric method just as selectively sensitive to the absorption wave-lengths of the heavy gas atoms as the plate in the photographic method exhibits sensitivity maxima for the absorption frequencies of silver and bromine. Another method to increase the sensitivity of the air ionization chamber without the simultaneous production of selective absorption consists in the utilization of high pressure chambers filled with air at several atmospheres' pressure. Fricke and Glasser have carried out very important experiments on the utilization of very small ionization chambers. As material for the metal parts they selected such combinations that the average atomic number of the material was exactly as large as the average atomic number of air. In this manner, they eliminated the selective influences of the chamber walls.

Knowledge of the mechanism of the ionization process by Roentgen rays is very important. Recent work by Kulenkampff has established definitely that gaseous ionization takes place in the following manner. A Roentgen ray quantum is absorbed by a gas molecule. As a result, the gaseous atom becomes ionized emitting thereby an electron whose kinetic energy, according to quantum principles, is equal to the energy quantum of the absorbed Roentgen ray, viz.: $\frac{1}{2}\mu v^2 = h \cdot \nu$. This electron is in very rapid motion and upon impact with other gas molecules ionizes them, whereby it gradually consumes its energy and loses its velocity. The formation of each pair of ions, on the average, requires energy equivalent to 35 volts. This amount of energy is independent of the wave-length of the absorbed radiation in the region of 0.56 to 2 Å., which is equivalent to saying that it is independent also of the velocity of the primary electrons.

In order satisfactorily to utilize the convenient photographic and ionometric methods for determining the absolute intensities it is necessary that both be compared to the energy method. In other words, the "darkening" and the ionization must be measured, respectively, per unit of absorbed energy.

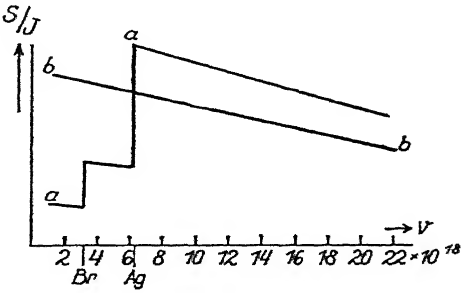

Fig. 44.

Comparison experiments to determine the intensities by the photographic and the ionometric methods were undertaken by Berthold and Glocker. From their data they concluded, for homogeneous Roentgen radiation of wave-lengths from 0.14 to 2 Å., that the ratio of "darkening" over intensity (S/J) was a linear function of the frequency, becoming smaller for increasing frequencies if absorption is kept equal. The curves (*a*) and (*b*) in Figure 44 show this dependence, the former being obtained when absorption is disregarded, the latter when due consideration is given absorption. We perceive here how the strong selective dependence on frequency totally vanishes if allowance be made for the selective absorption by the bromine and the silver of the photographic plate and that, for a frequency variation of 1 : 12, the quotient S/J varies by only 1 : 1.8. Kulenkampff declares that the small linear frequency dependence present in the linear S/J curves of Berthold and Glocker is absent in the region of the longer waves, if coefficients of absorption of air are used which have the following values according to calculations made previously by him.

In the region of wave-lengths above 1.8 Å., the exponent n of the wave-length in the equation μ/ρ = prop. λ^n is no longer 3, but 2.8.

Coefficients of Absorption of Air

λ Å.	μ/ρ	λ Å.	μ/ρ
0.3	0.073	1.2	4.50
0.4	0.173	1.4	6.91
0.5	0.348	1.6	10.05
0.6	0.597	1.8	14.0
0.7	0.960	2.0	18.9
0.8	1.40	2.2	24.5
0.9	2.00	2.4	31.2
1.0	2.70	2.6	39.1

Taking into consideration, therefore, the absorption coefficients of air, the ratio "darkening" to ionization S/J becomes more and more independent of the frequency.

A. Kulenkampff, thereupon, compared the ionization with the directly measured energy of the Roentgen rays and confirmed the correctness of the result obtained in 1906 by Angerer, viz.: that the ionization J is proportional to the absolute measured energy E of the Roentgen rays; he also verified the constancy of the ratio E/J for all wave-lengths between 2 and 0.56 Å. His experiments, furthermore, corroborated the correctness of the previously cited quantitative result that 35 volts are necessary for the formation of each ion-pair. The ionization current J, i.e., the number of ion-pairs, is obtained from the energy absorbed by the gas of the ionization chamber αE (where α is the coefficient of absorption) and the length of the absorption-path, l, as equal to $\alpha El/\epsilon$, where ϵ is the energy requisite for the formation of an ion-pair. A few results are listed in the following table showing the energy of ion-formation for monochromatic Roentgen rays (K-rays of the anticathode).

Anticathode	ϵ (Volt per Ion-pair)
Silver	35.7
Molybdenum	35.2
Iron	35.1
Platinum	34.3
Copper	34.6
Iron	35.6

The independence of wave-length is shown in the following Figure 45. Bouwers carried out comparative investigations on the photographic "darkening" S and the bolometrically measured energy in the region of shorter wave-lengths (from 0.7 to 0.2 Å.) and found a linear dependence of the quotient S/E on the frequency somewhat similar to that found in the same frequency region by Glocker and Berthold. This is evident from Figure 46, in which the values obtained by Bouwers (indicated by the cross-marks) coincide within the 10 per cent allowable accuracy with the S/J curve of Berthold and Glocker. But if S/J and S/E show the same dependence on frequency, it follows that the ratio J/E is independent of the wave-length, which is, in fact, the result of the direct measurement of Kulenkampff in the region up to 0.5 Å. and valid, therefore, for shorter wave-lengths down to 0.1 Å.

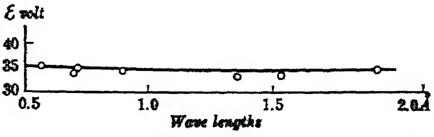

FIG. 45.

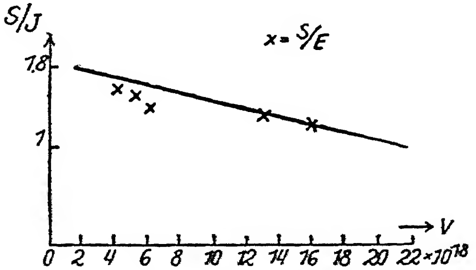

FIG. 46.

We shall take up again our consideration of the investigations of the continuous Roentgen spectrum.

Kulenkampff investigated the dependence of the distribution of spectral intensity on the metal of the anticathode (Al, Fe, Co, Ni, Cu, Ag, Sn, Pt) by measuring the energy perpendicular to the direction of the cathode ray up to 10,470 volts, and for platinum and silver, the dependence on potential over a potential range of 7–12 kilovolts (minimum wave-length 1.8–1 Å.). Utilization of a gas tube made it necessary to base the measurement of the energy of the cathode ray not upon the current strength as measured by the milliamperemeter, since this is composed of ionic and electronic streams, but upon the calorimetrically determined heat imparted to the cooling water of the anticathode, which depends solely upon the electronic current concerned in the Roentgen ray excitation. Since the ion-chamber method again gives correctly the true energy distribution, we may consider these measurements in the selected potential range as final and conclusive, owing to the consideration given to disturbing influences as described above. Among the older researches that of Ulrey[10] deserves special mention because it was considered, until recently, the most reliable and because it suggested conjectural points for theoretical discussion.[11] This experimenter investigated by means of a Coolidge tube the intensity dependence on atomic number; six metals were thus studied at 35 kv., some of which are shown graphically in Figure 47; here, the independence of the short wave end of the intensity curve of the material of the anticathode is depicted for tungsten, molybdenum and chromium. Following this, the dependence on potential was measured for the range 20–30 kv., using tungsten as the anticathode material. Ulrey deduced several "regularities" which in part confirmed earlier data, but failed to arrive at a definite conclusion regarding them. He found a formal analogy to Wien's displacement law (thermal radiation theory) in deriving the relation $\lambda_{max.} V^{1/2}$ = constant, where $\lambda_{max.}$ has the same significance as in Wien's law, $\lambda_{max.} T = b$. For total radiation a proportionality was found to the square of the tube potential, i.e., to the fourth power of velocity of the cathode rays (Stefan-Boltzman, $S = \sigma T^4$), and, finally, a proportionality to the atomic number of the an-

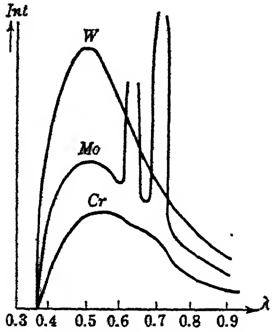

FIG. 47.

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[10] C. T. Ulrey, Phys. Rev. 11, 401 (1918).

[11] March, Phys. Zeitschr. 22, 209 and 429 (1921). Behnken, Zeitschr. f. Phys. 4, 241 (1921).

ticathode material. The last mentioned result has been verified definitely by Kulenkampff Fig. 48). The dependence of the total radiation upon the square of the potential may also appear certain, even though the rather recent work of Bouwers cannot yet be considered conclusive. Remarkable supplementary data are furnished by another extensive study by Kulenkampff. The problem may be viewed most simply by means of the formulæ derived in the original research (loc. cit.):

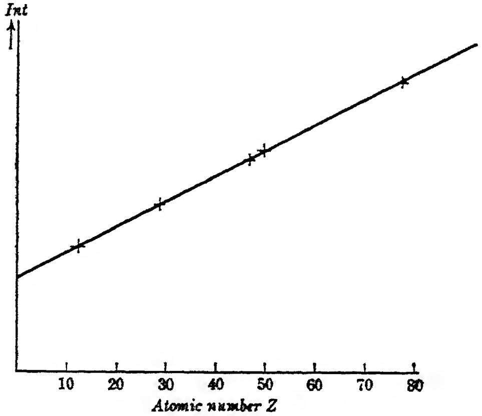

Fig. 48.

$$J_\nu = \text{const. } \{Z(\nu_0 - \nu)Z^2 \cdot b\},$$

$$J = \int_0^{\nu_0} J_\nu d\nu = \text{const. } \{Z\nu_0^2 + bZ^2 \cdot \nu_0\}$$

$$= \text{const. } \{Z \cdot V^2 + bZ^2 \cdot V\},$$

$$\lambda_{\text{max.}} = \frac{3}{2} \frac{\lambda_0}{1 + \frac{b}{c} Z\lambda_0}, \qquad \frac{\lambda_{\text{max.}}}{\lambda_0} = \frac{3}{2} \frac{V}{V + K\frac{b}{c} \cdot Z},$$

where ν_0 and λ_0 designate respectively maximal frequency and minimum wave-length, related, according to the Duane-Hunt law, to the tube potential V; b and c are constants. We may summarize, therefore:

1. The total intensity is intrinsically proportional to the

atomic number Z and to the square of the potential, a portion, however, being proportional to the potential and to the square of the atomic number of the anticathode material.

2. For constant potential $\lambda_{max.}$ will be displaced to shorter wave-lengths with increasing atomic number Z.

3. $\lambda_{max.}/\lambda_0$ is inversely proportional to the atomic number Z and approaches progressively to the limiting value $3/2$ with decreasing Z and increasing potential, whereas Ulrey finds $\lambda_{max.}/\lambda_0$ proportional to $V^{-1/2}$, as may be determined from $\lambda_{max.} \cdot V^{1/2} = \text{const.}$

Indeed, it seems questionable whether any special significance should be attributed to the value of $\lambda_{max.}$; in any event, however, the minimum wave-length of the Roentgen spectrum plays the characteristic rôle of the $\lambda_{max.}$ in the thermal spectrum.

Thus far we have discussed only the continuous Roentgen spectrum; we must now enter into a brief discussion of the characteristic spectrum, whose intensity masks that of the continuous spectrum, and, under certain circumstances, renders its recognition extremely difficult. Older researches produced the impression that the emission of the characteristic radiation would influence the adjacent portion of the continuous spectrum in the direction of short waves. Following Weber, the opinion was propagated that the energy of line radiations was derived from this portion of the energy of the continuous spectrum. Contrary to this conception, which appeared very plausible in the light of Stokes' law, Wagner, amongst others, expressed the opinion that the observed decrease in the intensity in the continuous spectrum may be attributable to absorption in the anticathode, which, as is well known, takes place appreciably close to the specific vibrations, particularly so upon the high frequency side of the spectrum. This latter viewpoint was confirmed definitely by Kulenkampff, thereby clearing up this disputed problem. To be sure, both these viewpoints are not mutually exclusive, inasmuch as a portion of the absorbed energy is transposed into specific radiation which augments the specific radiation primarily due to stimulation by cathode rays.

Attention may be directed to two other investigations[12] from which it follows that the form of the intensity curve is independent of the current strength and that it is modified but slightly by utilization of alternate current in place of a constant battery potential. March finds the cause of the latter observation in the decrease in intensity furnished by low potentials, as opposed to the intensity of the potentials adjacent to the "peak" value (the proportional relation between J and V^2 is important at this point), and furnishes calculations to justify this consideration.

If we summarize briefly our experimental knowledge of the continuous Roentgen spectrum, we must mention the Duane-Hunt law as paramount in importance. In addition, we have the distribution of the spectral intensity as being universal for all cathode metals and determined only by the tube potential. The absolute value of the intensity depends upon the atomic number of the anticathode material and the strength of the electronic stream and the potential.

Theoretical treatises on the continuous Roentgen spectrum based upon the quantum theory have been developed by H. Behnken,[13] A. March,[14] G. Wentzel, and others.

The measurement of the absolute intensity of the total Roentgen spectrum of an anticathode makes possible the determination of the "efficiency" of the Roentgen stimulation, i.e., the quotient of the Roentgen ray energy to the cathode ray energy, a problem solved correctly as early as 1905—as is evident—by W. Wien. These efficiency values naturally are dependent upon the potential, since the Roentgen ray energy is proportional to the square of the potential and the cathode ray energy proportional only to the first power of the potential. Furthermore, the radiation is proportional to the atomic number of the element used in the anticathode. We have, therefore, the relationship

$$\eta = \frac{\text{Roentgen ray energy}}{\text{Cathode ray energy}} = \eta_0 \frac{J \cdot Z \cdot V^2}{J \cdot V},$$

[12] Behnken, Zeitschr. f. Phys. 3, 48 (1920). March, Ann. d. Phys. 65, 449 (1921).

[13] Behnken, Zeitschr. f. Phys. 4, 241 (1921).

[14] March, Phys. Zeitschr. 22, 209 and 249 (1921), 23, 84 (1922).

wherein J designates the cathode ray current, Z the atomic number, and V the cathode ray potential. The measurements of three observers are given below:

W. Wien	$V = 58{,}700$ volts	$\eta_0 = 5.9 \times 10^{-10}$,
Bouwers	30,000 to 100,000 volts	5.6×10^{-10},
Aurén	50,000 to 100,000 volts	7×10^{-10}.

Thus, for a platinum anticathode ($Z = 78$) and a potential of 50,000 volts, η would become

$$\eta = \eta_0 \times Z \times V = 6 \times 10^{-10} \times 78 \times 50{,}000 = 0.23 \text{ per cent.}$$

The quantum theory finds an important practical application for the excitation of the short wave end of the continuous Roentgen ray spectrum in the so-called potential measurements by spectroscopic means. By the displacement law of Duane and Hunt, according to which the limiting wavelengths of the continuous Roentgen spectrum vary independently of the emitting material with the excitation potential V of the Roentgen rays (V is, therefore, the volt-velocity of the electrons) according to the equation $\nu_{\text{max.}} = \epsilon V/h$; $\lambda_{\text{min.}} = ch/\epsilon V$, we will obtain for the potential applied in the Roentgen tube yielding a continuous spectrum to the wave-length $\lambda_{\text{min.}}$ the numerical value

$$V = 12.3/\lambda_{\text{min.}} \text{ kilovolts.}$$

The practical utility of this method, discussed fully by Seeman and Küstner particularly, has been confirmed by the recent investigations of Glocker and Kaupp.[15] Their procedure is somewhat as follows: by means of a Seeman X-ray spectrograph, spectral photographs are made which show the line spectrum and the continuous spectrum. With appropriate darkening of the latter, it will suffice to measure the distance of the end of the continuous spectrum to a definitely known line by means of a rule or simple micrometer

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[15] Radiation Therapy, XXII (1926), p. 160.

microscope. Furthermore, the dispersion in spectral range utilized must be known. If 1 mm. on the plate corresponds to a wave-length difference of α Å., and if the limiting line of the spectrum is distant l mm. from a spectral line of wave-length λ, the minimum wave-length, i.e., the short wave boundary length of the continuous spectrum, will be calculated as $\lambda_{\text{min.}} = (\lambda - \alpha \times l)$ Å.

It is important, therefore, that Glocker and Kaupp were able to show that this limiting wave-length could be determined, independently of the extent of darkening, of the type of plate utilized, as well as independently of the width of the spectrograph slit, with such accuracy that an error of more than a few per cent for the excitation potential may be eliminated. With a good photometric method, a still greater accuracy may be obtained; thus, for example, the results obtained in measuring a potential of about 183 kv. varied between the limits 180.1 and 184.4 kilovolts. The significance of this procedure for measuring extremely high potentials is obvious.

CHAPTER XV

SPECTRAL EMISSIONS AND THE PERIODIC SYSTEM

Originally spectral analysis had a chemical application only: to establish evidence of the presence of an element by the observation of its characteristic spectral lines. Today its task is more generally extended, the field of its activity having become more expansive and consequently more significant. Thus, the spectrum of an element yields evidence not only of its chemical nature but it reveals, more or less completely, an insight into the physical condition of the emitting atom. For quite some time a distinction has been drawn between "arc" and "spark" spectra. These differ one from another exteriorly since the spectral lines emitted in the "spark" discharge are wanting in the arc spectra. On the other hand, lines of high prominence in the arc spectrum are absent or faintly visible in the spark spectrum. In the light of our recent experimental data we designate the spectrum of the normal atom as its arc spectrum, while the spark spectrum is attributed to its ion, i.e., to the atom when electrified with a single positive charge. Although this view has been accepted for some time as plausible and expressive of facts from indirect reasoning only, recent experimental data happily and amply confirm its correctness.[1]

Furthermore, the excitation energies of the spark spectra have been determined; in several instances this has been accomplished directly by means of the electronic impact method. It was found that very high volt-velocities—about 80 volts—were necessary to excite the helium spark spectrum.[2] Excitation of the spectra of the alkali ions may be accomplished with smaller energies, but nevertheless these are still relatively high, comparable to or even larger than that

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[1] W. Wien, Ann. d. Phys. 69, 1 (1922).

[2] The first excitation measurement is due to H. Rau (1914).

requisite for the stimulation of the spectrum of the neutral noble gases. The ions of the alkali-earths, however, part with their second electron very rapidly, approximately twice the requisite work for primary ionization being necessary for the secondary ionization. Tertiary ionization has not yet been observed for them. The elements of the third group in the periodic system, on the other hand, can experience still one more ionization stage. The number of possible ionization stages peculiar to any element is thus equal to the number of its chemical valence electrons.

We shall base our conceptions fundamentally upon the notion that an element is characterized by its ordinal number (atomic number). Numerically, this designates the number of free positive charges within the nucleus, and in the case of the neutral atom it equals also the number of free electrons in the atom. Let us consider the elements seriatim as they follow upon one another in the periodic system. Suppose a definite number of electrons to be specified by Z; then, the normal condition of the atoms of the noble gases may contain within its structure Z electrons, the alkali elements $Z + 1$, the alkali earths $Z + 2$, and the earth $Z + 3$. These numbers are, therefore, the ordinal numbers of the elements and indicate their respective positions in the periodic system. If an alkali atom is transformed into its ion, which happens upon the withdrawal of one of its electrons, it still retains within its structure Z electrons; the electronic structure of the alkali elements thus presents the habitus and configuration peculiar to the immediately preceding inert gas. Upon this is based, of course, a great portion of Kossel's theory of molecular structure as well as the development of the laws of atomic structure according to N. Bohr.

To determine how their respective spectra make observable the transformation of the habitus of the alkali elements into that of the inert gases we must first consider somewhat more thoroughly the spectra of the several alkali atoms. Close scrutiny of the spectral lines observed for the alkali atoms (whatever may be mentioned in the sequel regarding the alkali elements applies likewise to the second family of the univalent elements, copper, silver, gold) discloses that nearly all the lines are "double," i.e., they consist in reality of two almost coincident lines. Such lines are termed "doublets." The two D-lines of sodium, D_1 and D_2, present a typical example of a doublet. The arc spectra of all alkali elements show evidences of the presence of doublets, but the difference between the wave-lengths of the doublet lines is not the same for all elements, the difference becoming more marked with increasing ordinal or atomic number of the element. In other words, the doublet lines become progressively more and more separated. The spectral lines of the alkalis corresponding to the D-lines of sodium have wave-length differences as given below:

	λ	Δλ
Li	6,708	0.151 Å.
	6,708	
Na	5,890	6 Å.
	5,896	
K	7,665	34 Å.
	7,699	

The metals of the second family of the first vertical group (copper, silver, gold) likewise have spectra characterized by "doublet systems." The spectra of the alkali earths, on the other hand, exhibit an entirely different character; they are marked by the appearance in them of groups of three lines each, the so-called "triplet-lines." As in the case of the doublet lines, the wave-length differences of these triplet systems increase progressively with increased ordinal number of the alkali earths. Thus, corresponding "triplet lines" for magnesium, cadmium and mercury and their respective wave-length differences are:

Magnesium		Cadmium		Mercury	
11	5,184 Å.	185	5,086	1,103	5,461
	5,173		4,801		4,358
5	5,168	123	4,678	311	4,047

But not all lines of these elements belong to such triplet systems. Paschen has discovered in the spectra of alkali earths a series of single lines in addition to the triplet-line series, these lines being equally characteristic of, and peculiar to, the arc spectra of the metals.

If we turn now to the spectrum of aluminum, an element of the fourth vertical group, the earths, we will note therein a recurrence of doublet lines, similar in type to those observed in the spectra of the alkali metals.

But what about the spectra of the inactive gases of the "zero group" in the periodic system? Helium yields a spectrum showing simultaneously a system of single lines and a doublet system. Its series of doublet lines,[3] however, is of an entirely different type from that found for the alkali elements. It is extremely likely that this is composed actually of three lines of almost equal wave-lengths, i.e., a triplet series, which is mistaken as a doublet because of the low resolving power of the spectroscopes hitherto available.

Synopsis of these data leads to the Kossel-Sommerfeld displacement law: the spectra produced by the elements in a given horizontal row of the periodic system show an alternate recurrence of triplets and single line series and doublet systems; that is, the elements of the vertical groups 0, 2, 4, · · ·, yield triplet and single line series, while the groups 1, 3, 5, show doublet lines.

What has been said thus far applies only to the spectra of the electrically neutral, the normal, atoms. Let us now compare the spark and the arc spectra of corresponding elements. The spark spectra of the alkalis have not yet been investigated to any considerable extent. As far as definite analysis of these spectra will permit, their lines show the character of the spectra obtained for the normal atoms of the inert gases. The spark spectra of the divalent elements, the alkali earths, are known likewise and have been grouped, in part, in series; all yield, in place of the triplet series of the normal atom, a doublet system peculiar to the ionized atom.

[3] Recognized by the splitting of the line in a magnetic field.

Still different data are obtained in the case of aluminum, the most thoroughly investigated representative of the third group of the periodic system, the earths. Although its arc spectrum shows a doublet system, its first spark spectrum consists of triplet series. These observations may be formulated collectively in the spectroscopic displacement law. They furnish us with a surprisingly clear notion of the configuration of the exterior electrons of the atoms. Let us take, for example, the alkali earth possessing $Z + 2$ electrons. Its arc spectrum shows a triplet system. Upon experiencing a primary ionization by the removal of one electron, it will still retain within its structure $Z + 1$ exterior electrons; its exterior habitus will thus become similar to the electronic configuration of the alkalis as will also its spectrum. The ionized alkali earths with their residual $Z + 1$ electrons will thus display the same spectrum type as the normal alkali containing the same number of electrons $(Z + 1)$. Similarly, the earth, with $Z + 3$ electrons, when ionized, becomes similar to the alkali earth with $Z + 2$ electrons in somewhat the same manner as its spark spectrum corresponds to the arc spectrum of the alkali earth since both now possess the same number of exterior electrons. Further ionization, i.e., the removal of a second electron, will transform the external habitus of the earth to $Z + 1$ electrons and its spectrum will be a typical alkali spectrum showing the normal doublet system peculiar to the alkalis. These facts may be generalized somewhat as follows:

Group of the periodic system	0	1	2	3	4
Atomic number	Z	$Z + 1$	$Z + 2$	$Z + 3$	$Z + 4$
Normal atom	Triplet	Doublet	Triplet	Doublet	Triplet
Univalent ion		Unknown spectrum anal. alkali			
Divalent ion			Unknown	Doublet	Triplet
Trivalent ion				Unknown	Doublet

Elements thus far investigated are given below. Atoms and ions in the same vertical column show the same spectral type.

Argon	Potassium	Magnesium	Aluminum	Silicon
Potassium$^+$	Magnesium$^+$	Aluminum$^+$	Silicon$^+$	
	Aluminum^{++}	Silicon^{++}		
	Silicon^{+++}			

It was remarked at the outset of this chapter that the physical spectral analysis of elements is more informative than is a chemical spectral analysis inasmuch as it reveals definite data regarding the physical condition of the atom over and above a qualitative proof of its presence. Thus, we have seen that physical spectral analysis correlates the exterior configuration of an atom with its chemical valence. It demonstrates above all else the equivalence or the identity of those electrons which are designated as "valence electrons."

It has not been possible, to date, to demonstrate successive ionization stages in excess of the chemical valence of the atom; not even the application of relatively great energies produced evidences of "higher ionizations." We may ask, however, what changes may "higher energies" induce within the atom? In answer, we must return to a subject already discussed rather fully and in detail in Chapters XIII and XIV, the topic of X-ray emission. Under the influence of "higher energies" the atom is stimulated to X-ray emission. Part of this complex emission, it will be recalled, is typical and peculiar to the "excited" atom. There are certain lines, whose positions in the spectrum, i.e., whose wave-lengths, are characteristic marks of a chemical atom. A chemical X-ray spectral analysis is thus very feasible, such spectra having already been variously investigated and tested. Under certain conditions X-ray analysis has a decided advantage over ordinary chemical and spectral analyses. Chemical analysis and chemical spectral analysis both transform the "analyzed" body into different forms; they "destroy" the body. X-ray analysis, on the other hand—though applied at first only to solids—in no way alters it. When made the anticathode in an X-ray tube, the body emits, under bombardment of cathode rays, definite frequencies whose wave-lengths are peculiar to its chemical atomic constituents and which can be photographed and measured; or it may be brought as an absorbing medium into a continuous X-ray spectrum, in which condition wave-lengths peculiar to its structure will be absorbed. The positions of the spectral lines, i.e., their wave-lengths, alone are characteristic of the element. All elements show the same general type of X-ray emission. The relative position of the spectral lines is independent entirely of the chemical character of the element and of the mode of chemical combination of the element in a molecule.[4] This furnishes us with a new key to the structure of the atom. X-rays are emitted by electrons which evidently play no part in the chemical behavior of an atom, that is, by electrons which are situated more deeply within the atom than are the exterior valence electrons or "photoelectrons." Their localization is the same for all elements, all traces of periodicity having vanished, the progressively increasing structure of the atoms taken seriatim alone coming into play. The excitation energies requisite for these X-ray series are conditioned solely upon the atomic number, the nuclear charge, of the elements. The excitation energy increases with the positive charge upon the nucleus.

And finally, that X-ray excitation consists in the removal of an electron from its normal orbit to a higher (farther removed) orbit is indicated by the boundary of an X-ray series. As in optical series a continuous absorption is associated with it with a simultaneous and complete removal of an electron from the atom, i.e., it is ionized.

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[4] We merely refer here to the difference of the Roentgen spectra of allotropic modifications, e.g., of the various forms of phosphorus. These differences are apparent in the lighter atoms, in which the difference between "inner" and "exterior" electrons is less marked because of the paucity of electrons.

CHAPTER XVI

EMISSION AND ABSORPTION PHENOMENA TAKING PLACE WITHIN AN ATOM ON THE BASIS OF BOHR'S THEORY

We will not discuss in this chapter the tenets of Bohr's atom theory;[1] nor do we propose to consider the theoretical conceptions upon which these tenets are founded. Since, however, this theory of the atom has so successfully stimulated highly productive experimental investigations, the like of which had not been accomplished by previous theories; and since it has presented an entirely new viewpoint and offered new methods of attack for many hitherto frequently discussed problems of spectroscopy, it will be expedient for us to review the salient features appertaining to this theory in a brief schematic manner.[2]

Thus, it is postulated that the atom is so constructed that electrons are in constant motion about an inner nucleus in which are associated its mass and positive charge. The number of these rotating electrons is given by the atomic number of the element, i.e., its ordinal number indicative of its position in the periodic system; for example, 1 for hydrogen, 3 for lithium, and 80 for mercury. These electrons are termed "exterior electrons" as opposed to other electrons localized within the nucleus itself. The atom, per se, is always electrically neutral; i.e., the number of its exterior electrons is equal to, and compensates, the number of "free" positive charges associated with the nucleus. We use the word "free" advisedly because a greater number of positive

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[1] See A. Landé, Wissenschaftliche Forschungsberichte, Vol. 5 (1926).

[2] It is important to emphasize the fact that the theoretical laws are in a certain sense merely model in character, based upon a few more or less clearly recognized natural laws. Most of the specially specific laws are founded upon concepts, e.g., that of "quantum numbers" whose heuristic advantage is apparent without a doubt, but whose physical meaning is entirely unknown to us. Only in the theory proposed by Schroedinger does a natural explanation of "quantum numbers" seem evident.

charges are inherent in the nucleus than is indicated by the atomic number. Yet, some of these positive nuclear charges are "bound," i.e., compensated for, by the electrons present in the nucleus, the so-called inner or nuclear electrons. The hydrogen nucleus is adopted as the unit of the electrically positive mass. Helium (of mass = 4) has but two exterior electrons according to its ordinal number. Obviously, to balance the two remaining positive charges, electrons must be situated within its nucleus which in turn may be considered as being composed of 4 positive hydrogen nuclei (4H). The number of exterior electrons and the magnitude of the free positive charges within the nucleus determine the positions of the various elements in the periodic system and also their respective chemical deportment. Their relative "masses" and numbers of nuclear electrons are unessential for this classification. (See Chap. II.)

The statements made thus far as to the number of electrons present in the several atoms are based upon and epitomize the data of very accurate experimentation. Moreover, it is possible, from the data of X-ray investigation, to make fairly definite statements regarding the respective positions, or better, the orbits of the exterior electrons. The electrons revolve about the nucleus in orbits peculiar to themselves, a definite number of them tending to form in groups. The net effect of such correlation is the "surrounding" of the nucleus by a number of concentric occupied shells, each shell being capable of containing only a limited number of electrons.[3] Furthermore, each electron in such a shell is characterized by a specific energy content proportionate respectively to its distance from the nucleus, the magnitude of the nuclear charge and the number of electronic shells intervening between it and the nucleus. We may, accordingly, substitute for the expression "electronic shells" the term "energy level" which is not conditioned upon any special spatial model.

[3] We will not consider here the penetration of the orbits, whose basic explanation may be considered as definitely established. (See Schroedinger, Zeitschr. f. Phys. 4, 347 (1921); N. Bohr, Nature (1921).)

Granting, then, that the electrons of the normal atom are individually localized in definite energy levels, Bohr's theory of the emission and the absorption of radiation postulates that an electron cannot assume every random position upon its withdrawal from its specific orbit so long as it still remains within the sphere of influence of the positive electric nuclear forces. In other words, the atom absorbs energy, not at random, but only certain very definite and characteristic energies which vary from atom to atom. The transference of an electron from its normal orbit to another orbit (or to transform an atom from its normal state to a more energetic condition) is designated as "excitation" of the atom. If the transferred electron originates from one of the exterior shells, the atom is spoken of as being "optically excited"; on the other hand, if the electron is situated in one of the inner spheres, i.e., closer to the nucleus, the atom is stimulated to the emission of X-rays. The simplest type of atomic excitation consists, thus, in the transfer of an electron to a higher orbit, i.e., to a higher energy level, the requisite energy for this transfer, the so-called "excitation energy" being "absorbed" by the atom; the "excited" atom retains this "absorbed" energy as potential energy. Under these conditions, with the excess energy stored within its structure, the atom no longer is stable and tends to release it. If, therefore, this energy is disengaged subsequently by the atom, i.e., if the electron is restored from the "higher level" to its normal level (or generally to any other lower energy level, the normal being the lowest and limiting level), the difference in the energy content of the two states will be emitted as a radiation. According to Bohr, this should be a monochromatic radiation, a spectral line, whose wave-length is determinable by the quantum theory.

The quantum theory states: if a radiation of frequency ν (frequency and wave-length being related to the velocity of light c by the expression $c = \nu\lambda$) is emitted, the energy E being measured in the calorimetric units, gr. cal., there will be contained, in this energy E, n quanta of the magnitude $h\nu$, where ν designates the frequency of the emitted radiation and h is Planck's universal constant. Whenever, therefore, a radiation of a given frequency ν is emitted, the energy incidental to its emission will contain at least one such quantum $h\nu$, or some multiple of it. Since h is a constant, the radiation energy of a definite radiation as well as its effectiveness is conditioned solely and unequivocally upon its frequency.

According to Bohr's quantum law, therefore, the energy difference between the excited and the normal atomic states $E_A - E_N$ is equal to a quantum $h\nu$; that is, the frequency of a given emission may be obtained from the relationship

$$\nu = \frac{E_A - E_N}{h}.$$

This is Bohr's frequency equation. From these considerations the two most conspicuous attributes of the spectral emissions of atoms become manifest to us immediately; thus, atoms emit only discrete and fixed wave-lengths because only certain excitation stages (energy states) are possible to them; and secondly, every atom emits its characteristic spectral lines because the number of the "excited" states possible to it depends upon the number of electric charges present in it and upon their relative orientation and grouping.

Two more facts of fundamental significance still remain for our consideration. It is a well-established fact that optical radiation and X-radiation do not differ essentially from one another. Optically considered, both radiations differ merely in their respective wave-lengths. The wave-lengths of the optical spectra—i.e., not only the visible portion of it, but all that is explorable by normal optical methods, with diffraction gratings, prisms, etc.—lie between 3×10^{-2} and 5×10^{-6} cm.; for those close to the X-ray region it is 10^{-9} cm. In the sense of the quantum theory the radiations are distinguished by their energy quanta $h\nu$, which are, respectively, for the wave-lengths specified above, 6.5×10^{-15} to 2×10^{-7} ergs, as calculated from the term

$h\nu$, the value of Planck's h having been taken as $h = 6.54 \times 10^{-27}$ erg sec. From these relations it is obvious that correspondingly greater energies are necessary for the excitation of X-radiation than for the stimulation of ordinary optical radiation. Obviously, relatively small energy is requisite for the removal of an electron in the outermost energy level from its normal orbit; accordingly, upon the return from the excited into the normal atomic state, there will be released a proportionately small energy content, i.e., a radiation of small frequency or of large wave-length. More energy must be applied, however, to withdraw an electron from an inner shell, the more deeply situated the electron the greater the requisite energy; that is, more energy is imparted to the atom. Subsequent reconversion into the normal state will be attended by the emission of greater frequencies. It matters not how large these various energies may prove to be; their disengagement always takes place as a fixed quantum $h\nu$. The excitation energies, however, cannot be haphazardly selected, that is, the atom is not excitable by all energies. The atom may absorb only such energy amounts—and these are absorbed in quanta, i.e., as units—that are capable of transforming it to a higher energy state, or, to use the terminology employed thus far, such energies that may elevate an electron to one of its possible higher energy levels.

According to the quantum theory it is entirely immaterial in what manner this energy is imparted to the atom. Only one condition must be fulfilled: it is essential that the energy be imparted in a single "elementary process." In later considerations the electrical excitation of atoms produced by impacts of moving electrons will be especially interesting. For the moment, however, the excitation of atoms by means of radiation will be given first and prominent attention. This latter method consists in the assumption of radiation energy by the atom, i.e., it is an absorption process. Bohr's frequency equation is also applicable to this process. Absorption of monochromatic radiation of a frequency will transform the atom from its normal condition E_n to a definite excited state E_A in such a manner that the energy intake ΔE ($= E_N - E_A$) is equal to the absorbed quantum $h\nu$. It does not suffice, therefore, that the radiant energy E, requisite for stimulation, be merely imparted to the atom. It must be absorbed as a unit quantum $h\nu$. It is this peculiar mode of absorption that we have termed previously an "elementary process." Since the several states of higher energy E_A into which the atom is convertible (this is likewise true of the absorbable energy difference E) are conditioned upon the intrinsic nature of the atom, it is readily understandable, on the one hand, why just certain frequencies are absorbable and why the absorption and emission frequencies must coincide; on the other hand, it is equally patent why definite generalizations regarding atomic structure may be drawn from available spectroscopic data. There still remains a second condition for the absorption of a monochromatic radiation of frequency, e.g., by a gas, a metallic vapor: the frequency corresponds to a reciprocal transition between two very specific energy states. If the transition arises from an excitation, i.e., absorption of energy, the absorbing medium must contain atoms of that energy state capable of accepting this energy. Should the atoms—in a special case—be present in the normal unexcited state E_N, then, obviously, only those frequencies can be absorbed that will transform the atoms to such energized states E_A from which the normal atomic state may result, upon reversion, with the attending emission of frequencies

$$\nu = \frac{E_A - E_N}{h}.$$

These emission lines, corresponding as they do to the transformations of definite excited states into the normal atom, must be regarded as particularly characteristic of, and essential to, the atom. For this reason they are termed the "principal spectral series" of the atom or its "absorption series," the latter name designating the fact that only these lines are absorbed by the normal atom. Incidentally, we may realize how important it is to know the absorption spectrum of a gas or metallic vapor.

Whatever has been stated thus far regarding the reciprocal transformation of the normal atomic condition into one of its excited states is valid likewise for the conversion of one excited state into another. There are special limitations, however, in each case; not all changes may take place in a normal manner; that is, there are certain excited states that are not convertible into other excited states; again, there are energized states which do not revert directly into the normal state with a simultaneous emission process. These states are explainable by certain principles of selection whose theory is unessential for us at this point.

Finally, there remains one more experimental result which will warrant discussion. Whereas a given atom can experience a transformation from one state into another only by a single "elementary process," provided of course that the available energy is sufficient thereto, its reversal can take place in intermediate stages,[4] i.e., with the emission of spectral lines of such wave-lengths that the sum of the respective quanta emitted during the successive stages is equal to the excitation energy. Or

$$h\nu_1 + h\nu_2 + h\nu_3 \cdots = h\nu = E_A - E_N.$$

The atom can revert directly, therefore, from state E_A to E_N by the emission of the frequency ν or by indirect stages by the emission of the several frequencies ν_1, ν_2, ν_3. We are now in a position to present schematically the absorption and emission processes involved in these changes. We will adopt the usual representation of "energy levels" as proposed by Sommerfeld since this involves no special postulate as to atomic structure; nor does it demand special assumptions regarding the series relationships or mode of designating the spectral lines of an atom, particularly the presentation of the emission of optical spectral lines; and of the frequencies emitted in the transition of an atom from an excited condition (or of an electron from a higher energy level) to

[4] Here also certain principles of selection are operative, which prohibit certain intermediate stages.

the normal state (or to the energy level of the unexcited atom).

The greatest energy difference available for emission results obviously when an electron has been removed to the extreme limit of the sphere of influence of the atomic nucleus as a result of imparted energy. We may express this by saying that the electron is at an infinite distance from the rest of the atom; the atom has lost an electron, i.e., it is ionized. The atomic residue constitutes a positive ion due to the abstraction of a negative charge, that of the electron. The energy necessary for such "infinite" withdrawal is one of the essential constants[5] of the atom; and it is readily apparent that its magnitude depends upon the intensity of the mutual and reciprocal attractive forces operative between the positive electric nucleus and the negative charge of the electron. It is termed the ionization energy of the atom and is designated by the symbol E_J. Upon the return of the electron from "infinite distance" to the "atomic ion" a correspondingly equal amount of radiant energy of such frequency will be emitted that $h\nu = E_J$; or the frequency of the emitted radiation is $\nu_\infty = E_J/h$.[6] This is, therefore, the greatest energy capable of emission by the neutral atom, i.e., its shortest spectral line: the ultra-violet end of the spectrum.

By convention the energy level at "infinite" withdrawal is designated by 0 and the other energy levels by numbers which give the energy differences in vibration numbers with respect to infinity according to the equation $\nu = \Delta E/h$ with negative signs. This sign is merely a matter of convenience; actually there is question merely of energy differences, the absorbed energies being taken as negative, the released

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[5] The constants met with thus far are: the free positive nuclear charge and the number of atom-electrons; the frequency of the absorption series; the ionization energy of the atom (equal to the boundary of the absorption series).

[6] For simplicity, it is assumed that the electron possesses no kinetic energy when exterior to the atom, just as we consider the individual atom and the ion ordinarily to be "at rest." Consideration of the kinetic energy in no way modifies the consideration of the excitation states; it comes into question only for frequencies greater than ν_∞.

energies as positive. In this way we arrive at the schema of Figure 49.

Here, 0 represents "infinite" removal, $-80,000$ is the outermost energy level of the normal atom, that is, "atomic surface." Between these two "levels" there is an energy

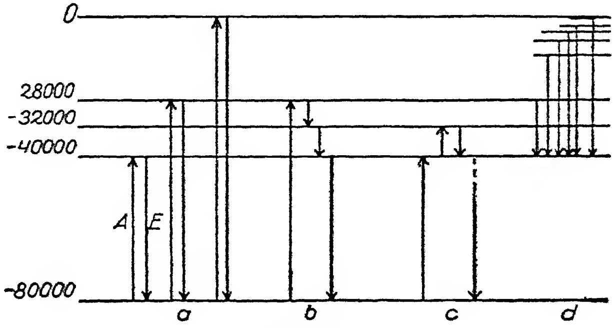

Fig. 49.

difference $E = \text{c.h.}\ (0 - (-80,000)) = \text{c.h.}\ 80,000$.[7] Only a limited number of other intermediate energy levels is possible. Some of these are shown in the diagram. Although the value $\nu = 80,000$ indicates obviously the highest and limiting frequency of the emission, the other lines of smaller frequency emitted during change from other excited states to the normal atom are indicated by the arrows of group (*a*) pointed downward toward the $-80,000$ level. The arrows marked *A* (pointed up) represent the absorption lines of the normal atom. Grouping (*b*) designates a very particular case in which excitation (up arrow) of the atom results through the absorption of frequency $+80,000 - 28,000 = 52,000$ in a "single" elementary process, whilst the emission may take place also in stages, as: $(32,000 - 28,000) + (40,000 - 32,000) + (80,000 - 40,000) = 52,000$, so that the energy balance $E_{\text{abs.}} = \text{c.h.}\ 52,000 = E$ emit. $= \text{c.h.}\ 52,000$ is again fulfilled.

The atom cannot revert directly from all excited states

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[7] The significance of these numbers will become apparent later. For the present, we mention merely that in the equation $E = \text{c.h.}\,\nu$, ν represents the wave number $\nu = 1/\lambda$, that is, the number of wave-lengths per centimeter, as is customary practice in spectroscopy.

into the normal condition; nor can it be transposed into these states by absorption. Such states, however, are closely associated with other states as is indicated, e.g., in grouping (*c*). Here the energy state corresponding to the level 40,000 was formed by energy absorption; the atom is subsequently transposed into the atomic state 32,000 by the absorption of frequency = 40,000 − 32,000; from this latter state the atom may revert to the normal level 80,000 by first stepping up to level 40,000 as an intermediate stage. Direct return from 32,000 to 80,000 in one emission act is not possible.

We thus have made clear the principles of our picture. We glean from it such simplicity and clarity which enable us to designate the spectral lines not only by their wave-lengths but also by their vibration numbers, that is, their wave numbers.

Spectral lines resulting from one and the same final level are termed and constitute a series. A spectral series contains, therefore, the spectral lines of an atom emitted by it during the changes of its various excited states into one given "final" state. Grouping (*a*) to the left of the diagram shows three lines of the so-called principal series (that series based upon the normal atomic state as its final condition); grouping (*d*) to the right indicates a spectral line series with respect to the state 40,000 as the "basic" level. Such series have definite types and have been given specific names, such as "sharp side series" and "diffuse side series." The energy levels designated numerically as above for a definite case are called "terms," so that each spectral line can be represented as the difference of two terms.[8] Attention may now be directed to another important relationship. It is evident from the two series designated above *a* and *d* that the limiting frequency (head) of series *a*, $\nu_{a,\,\infty}$, its first line $\nu_{a,\,1}$ and the limiting frequency of series $d \nu_{d,\,\infty}$ are related mutually according to the energy equation $\nu_{a1} = \nu_{a\infty} - \nu_{d\infty}$, which is likewise a frequency relationship according to the expression $\nu = E/\text{c.h.}$

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[8] For details see A. Landé, Wissenschaftliche Forschungsberichte, Vol. 5 (1926); F. Paschen and R. Goetze, "Series Spectra."

Similar examples are readily recognizable from the figure. They form the "combination principle" according to which each spectral line (measured in frequencies) is representable as the arithmetic sum of two others. This combination principle, which makes available one of the most important means of spectral analysis, i.e., the grouping of spectral lines in series, has been known empirically for a long time. This follows from the considerations introduced at this point, as the fundamental energy relation, bestowing a physical significance on the formal principle.

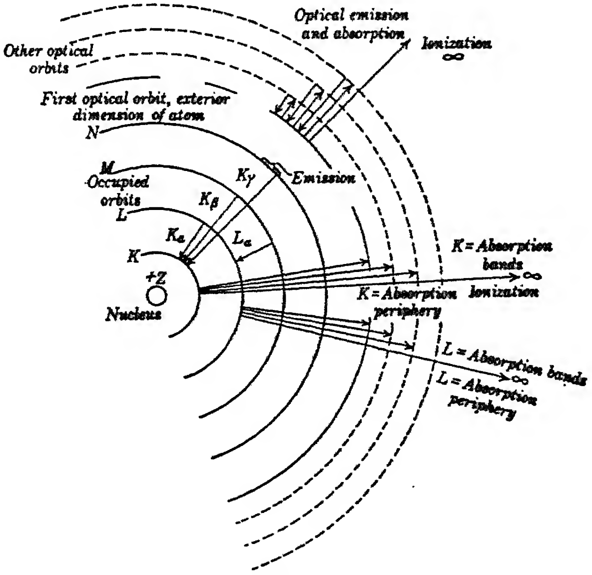

FIG. 50.

We append here a model survey of the entire emission and absorption process, of the "localization of the various radiations in the atom." Figure 50 represents an atom of high atomic number. Its nucleus Z is surrounded by the electronic groups (or shells) *K*, *L*, *M*, *N*. There is shown also the mechanism of the absorption and the emission of the principal optical series, the ionization stage, the emission of the K-series, the absorption of the *K* and *L* bands and the accompanying ionization whose frequency corresponds to the excitation energy of the corresponding Roentgen series. It must be emphasized at this point that we are concerned here with the absorption and release of energy and not, perchance, with "electronic leaps." The association of energy absorption with the removal of an electron from an atom (for optical radiation the removed electron is an exterior electron and for Roentgen radiation, an inner, nuclear electron) is established by the fact that the upper limit of every excitation consists in the complete removal of an electron from the atom, i.e., in the ionization of the atom. Upon this is based our conception of excited electronic orbits. Such a conception is, however, by no means necessary, as was noted in earlier chapters. For this reason we speak, as far as possible, only of energy changes within the total atom and not of its individual constituents.

One word more concerning the similarity in action obtained for different modes of producing the excitation energy. It is immaterial whether the absorbable energy is imparted to the atom in the form of electronic impact, by radiation or in the form of thermal energy—the atom is always transposed to the same excitation state. This does not apply so generally to molecules. Molecules primarily cannot be dissociated by electronic impact and by absorption of radiation, although this effect may be accomplished by thermal energy impacts. Excitation of a molecule by means of electronic impact or by radiation in no way affects an electron of the molecule. Thermal excitation, however, acts upon the atomic constituents of the molecule. This is most plainly apparent in the higher limits of the excitation possibilities. Whereas atoms are ionized in the "boundary" by radiation, electronic impact and thermal molecular impact, and molecules are likewise ionized by radiation and electron impact, the latter are dissociated by thermal energy.

CHAPTER XVII

RESONANCE AND DISPERSION
THE COMPTON EFFECT

Thus far we have confined our considerations to the excitation of electromagnetic radiation by means of electronic impact. It was inferred, in accordance with the fundamental principle of the quantum theory, that the frequency of the monochromatic radiation emitted during electronic impact may be calculated from the energy released by the electron according to the expression $\epsilon V = h\nu$. This phenomenon is most in evidence in the excitation of the continuous Roentgen spectrum: the short wave end, i.e., the high frequency end, of the spectrum is found according to this quantum relationship to be independent of all physical conditions, and particularly independent of the material of the emitting substance. The emission of more than one frequency is due to the fact that the total energy of an electron is not always transformed into Roentgen radiation during stimulation of the solid anticathode. It must be added also, as was explained in previous chapters, that for all excitations—of the optical spectral lines as well as of the characteristic Roentgen spectrum—the emission of a given frequency ν, by means of the energy of the electron ϵV, can occur only if the "excited" atom is capable of accepting this energy; that is, there is question here not only of the quantum law in regard to radiation but also in regard to atomic structure. As a fact, the knowledge of these possible frequencies serves to advantage in the analysis of atomic structure and atomic mechanics.

This law, however, in reality makes no definite pronouncement as to the nature of the stimulation or of a definite method in which the energy is imparted. It matters not in what manner the energy E is conveyed to an atom. The frequency of the emission always will be such that it will be related to E according to the expression $(E/\nu = h)$. King has established by particularly comprehensive evidence that metal vapors may be made to "glow" by addition of heat and that the spectral lines which appear first during such thermal excitation are exactly those which are first stimulated during electronic impact. The spectral emission of flames impregnated with metallic salts is the consequence of thermal excitation of atoms; if the relative velocity of any two colliding atoms is so large that the total energy of the impact suffices for the excitation of the frequency ν of one of the atoms, the atom so affected can be stimulated to the emission of this frequency.

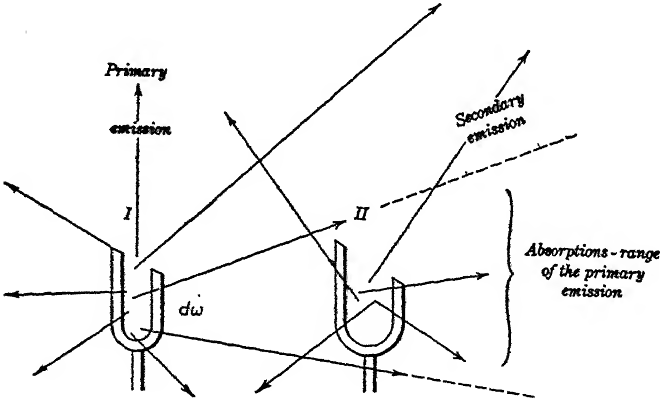

FIG. 51.

A third mode of stimulation is excitation by radiation. The re-emission of absorbed monochromatic radiation of the same wave-length as the absorbed radiation is termed "resonance radiation." The name "resonance radiation" is derived from its acoustic analogy, as is clear from the accompanying Figure 51. A tuning fork of known frequency is tapped; a second fork of equal frequency placed near the first fork will commence to vibrate in "resonance" with it. The first fork emits waves in all directions, and of these the second fork will absorb those that are contained in a definite conical space depending upon its size. It is thus brought into vibration and, in turn, emits the absorbed energy of the same wave-length in all directions. In this wise the radiant energy previously present in the conical space is dispersed, or scattered, in all directions. Figure 51 represents this phenomenon schematically. Optical resonance-absorption and emission proceed exteriorly in exactly the same manner. If tuning fork No. 1 is a luminous sodium flame and fork No. 2, non-luminous sodium vapor, the flame-emission from No. 1 will be absorbed in the angle $d\omega$, i.e., the yellow sodium D-lines of the vapor No. 1 present in the flame will not be visible through the vapor No. 2. Instead, there will be an emission from vapor No. 2, i.e., the Na-D-resonance emission, in all directions, including the angle $d\omega$. The secondary emission from No. 2 confined in the space $d\omega$ naturally will be much weaker in energy content than that radiated directly from No. 1 within the same space. This is obvious, since the latter serves as the energy source for the total energy emitted in all directions by No. 2. Thus far the analogy to acoustic resonance is perfect.

The difficulties attending such an explanation become apparent as soon as we consider the phenomenon from a quantitative point of view. It is known from experiments on resonance radiation that the absorbed energy is transposed completely into resonance radiation, there being no loss of energy due to transformation into heat. First, as regards the absorption process: according to the classical electron theory, an electron of the absorbing vapor takes up (absorbs) the radiation by being made to vibrate in progressively increasing amplitudes by the vibration of the primary ray.

According to the quantum viewpoint one atom of vapor No. 1 emits one light quantum $h\nu$ while one atom of vapor No. 2 absorbs this quantum, i.e., the atom absorbs the energy $E = h\nu$ because the latter is of such magnitude as to be absorbable by the atom; furthermore, this energy absorption proceeds in a similar manner as the absorption of an equal electron energy $E = \epsilon V$. As a consequence, the atom is elevated to a new, a more energetic state—the same state to which it is transposed upon electronic impact—and subsequently during its reversion to the normal state it will emit this quantum $h\nu = E$, in one direction or other, that is, it will reemit the primary frequency. Very little is known definitely regarding the exact direction of this emission. Because of the many individual actions arising in this experiment, every direction is present. In other words, the resonance radiation is of equal intensity in all directions.

This is the extreme viewpoint of the quantum theory of light. We need not stress particularly the momentary incompatibility of this viewpoint with that of the wave theory. It is almost impossible for us to doubt its reality,[1] however, since this viewpoint is established far more securely than on the resonance radiation alone. According to our conception the emitting atom ejects a quantum of light in a given direction. Consequently the atom will experience, according to the fundamental laws of mechanics, a recoil in the opposite direction. The magnitude of the recoil is imperceptibly small. We have still another method of dispersion which is very similar to the optical resonance method; viz.: the so-called dispersion of Roentgen rays.

It is known ever since Roentgen's first experiments that all bodies upon which X-radiation has fallen themselves become active and radiate Roentgen rays, i.e., they become "secondary radiators." This secondary radiation contained both the primary Roentgen radiation as well as the characteristic radiation of the secondary radiator. The influence of the latter may be eliminated by utilizing as secondary radiators bodies of low atomic weight (as carbon) whose characteristic frequency is of such long wave-length that they may readily be screened off during measurement of the secondary radiation. It is known, likewise, that the "hardness" of the secondary radiation is less pronounced than that of the primary radiation. As long as "hardness" measurements

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[1] Bohr, Kramers and Slater recently attempted to reconcile these opposing viewpoints.

and estimations of the mean wave-length ranges of Roentgen radiation could be made only by means of absorption experiments, the change in distribution of the spectral energy during dispersion remained a much discussed but nevertheless unsolved problem. Two possibilities were apparent. The change in the energy distribution may arise because the longer waves are favored during the dispersion process, or a change in wave-length may set in simultaneously with the dispersion. From the standpoint of the quantum theory the latter view seemed utterly impossible. However, a mechanical recoil of the electron was not taken into consideration, which, if taken up by a given electron, will consume a very appreciable amount of energy. A. H. Compton and P. Debye simultaneously carried on a discussion of this problem in connection with dispersion experiments of A. H. Compton. The unusually successful development of Roentgen technique in America has made it possible to examine the distribution of spectral energy of dispersed radiation by ionometric and by photometric methods. It was found that monochromatic radiation after dispersion contained, in addition to the primary frequency $h\nu$, a secondary radiation $h\nu'$ of smaller frequency, i.e., larger wave-length, than the primary radiation. It also is monochromatic, i.e., similar to a spectral line. This would be possible only if a small portion of the absorbed energy $h\nu$ is consumed for some other purpose, and the residual amount $h\nu'$ emitted. Such a process, however, would differ essentially from optical resonance since the wave-lengths are not kept constant; it would differ also from other normal fluorescences in that the fluorescence radiation is likewise monochromatic, and, finally, it differs from both phenomena in that the dispersing substance is entirely immaterial for the change in frequency. This fact indicates without a doubt that a general constituent, the electron, is involved as the dispersing agent.

The quantum theoretical explanation is as follows: a light quantum carries with it energy and impulse (radiation pressure). If a quantum is absorbed by a quasi-free electron (or one loosely bound in the atom) of the dispersing substance and subsequently re-emitted, impulse and energy will distribute themselves during the re-emission process upon a secondary quantum and electron according to normal mechanical calculations; the latter will experience a recoil, while the former is smaller than the primary quantum. The extent to which this will be smaller will depend upon the direction, with respect to the initial direction of the primary ray, in which the secondary quantum will continue The difference becomes greater with increasing angle of dispersion, i.e., the secondary radiation is of greater wave-length, the greater the dispersion angle. This dependence upon direction was discovered in 1923 [2] by A. H. Compton. Even though serious doubt has been raised during the last years as to the reality of this Compton Effect especially by reason of the negative results of Duane, nevertheless we may consider this effect as definitely established since Allison and Duane [3] have dropped their former objections on the ground of new and extremely carefully performed experiments. Repetitions of these experiments by Ross and Webster, as well as by Compton himself,

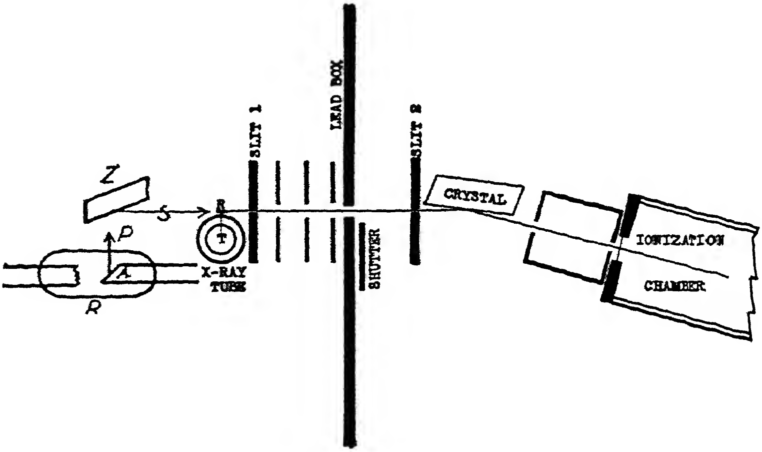

FIG. 52.

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[2] Physical Review 22, 409 (1923), or Phil. Mag. 46, 897 (1923).

[3] Allison and Duane, Proceedings of National Acad. of Sciences 11, 25 (1925).

more especially in conjunction with Woo, have established definitely the experimental result which is accepted today in many details because of a number of excellent investigations.

In principle the experimental arrangement is extremely simple. Radiation arising from the anticathode *A* (Fig. 52) of a Roentgen tube *R* is incident upon the dispersing substance *Z*. The secondary radiation proceeding from this passes through a slit into an ordinary spectrometer whose crystal *K* and ionization chamber (or photographic camera) are indicated in the diagram. Usually ionization methods replace the camera for measuring the radiation.

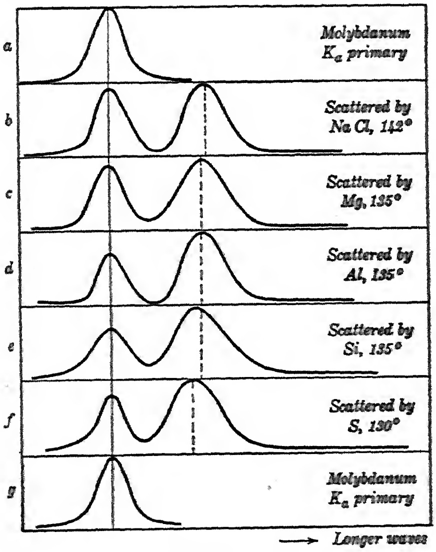

FIG. 53.

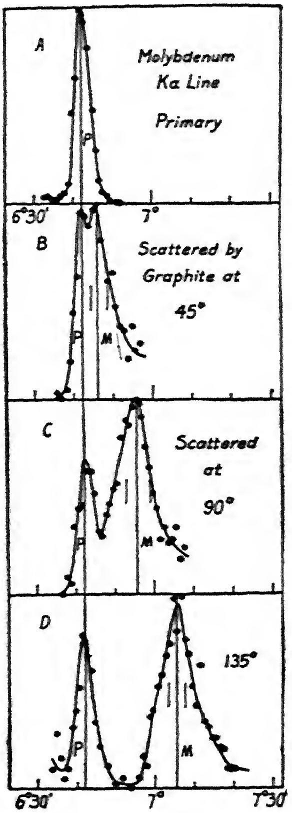

FIG. 54.

In experiments involving the use of the camera, illumination periods of 200–300 hours were necessary with anticathodes of molybdenum loaded with an alternating current of ~ 30 M.A. and 50,000 volts. The following Figures, 53 and 54, show the results of ionometric measurements; the former—taken later—is that of Y. H. Woo (in Compton's laboratory) and shows the distribution of intensity in the spectrum of the dispersed radiation for various dispersing substances under approximately equal dispersion angles: *a* and *g* are control experiments with the K_α radiation of molybdenum alone; the dispersed radiations of sodium chloride, magnesium, aluminum, silicon, and sulphur exhibit in addition to the molybdenum wave-length another radiation displaced toward the long wave end which is likewise monochromatic (although not as sharply as the undisplaced line). Figure 54, taken from one of Compton's first experiments, shows the measurement on the displacement of wave-lengths as functions of the dispersion angle.

This dependence on the dispersion angle is the really crucial fact; for the quantum theory predicts for this dispersion process the numerical values of this dependence on dispersion angle which are substantiated by experiment. The theory may be formulated very simply. We shall consider only the X-ray quanta which are "dispersed" by one electron, i.e., those that are absorbed and consequently re-emitted. If the frequency of this quantum be ν_0, its value will be $h\nu_0$, and its moment $h\nu_0/c$ (energy divided by the velocity of light). If the re-emission proceeds at an angle, the change in direction will bring about a change in momentum, i.e., the electron will experience a recoil of such extent that:

Recoil of electron = variations in moment of the quantum, or, expressed in a formula,

$$\left\{\frac{m\cdot\beta\cdot c}{\sqrt{1-\beta^2}}\right\}^2 = \left(\frac{h\nu_0}{c}\right)^2 + 2\frac{h\nu_0\cdot h\nu_\theta}{c^2}\cos\theta + \left(\frac{h\nu_\theta}{c}\right)^2 \left(\begin{matrix}\text{moment}\\ \text{relation}\end{matrix}\right).$$

where c is the velocity of light, βc the recoil velocity, m the mass of the electron, and $h\nu_0$ the quantum emitted in the direction θ. The second equation yields to the energy relation:

$$h\nu_0 - h\nu_\theta = mc^2\left\{\frac{1}{\sqrt{1-\beta^2}} - 1\right\}$$

as from both equations there follows directly

$$\nu_\theta = \frac{\nu_0}{1 + \frac{h\nu_0}{mc_2}(1 - \cos\theta)}.$$

Or

$$\delta\lambda = \lambda_\theta - \lambda_0 = \frac{h}{mc}(1 - \cos\theta),$$

$$\frac{h}{mc} = 0.0242 \times 10^{-8} \text{ cm.}$$

The directions of the primary X-ray, of the dispersed ray and of the recoil electron all lie in the same plane.

Kallman and Mark[4] recently performed very accurate photographic measurements of the Compton Effect in Berlin-Dahlem (Fig. 55). We cite their results here because they are particularly reliable: they dispersed the K-radiation of molybdenum by means of graphite at angles of 72° and 90°, and obtained the Compton lines for the dispersed K-line as well as for the K-line. The values obtained were:

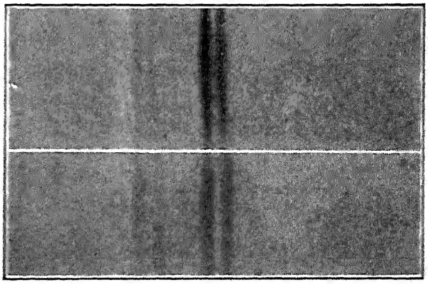

FIG. 55.

φ 72° $\delta\lambda$ (observed) 0.0170 Å. $\delta\lambda$ (theoretical) 0.0168 Å.

φ 90° $\delta\lambda$ (observed) 0.0241 Å. $\delta\lambda$ (theoretical) 0.0243 Å.

The theory thus explains the required dependence of the Compton dispersion on dispersion angle. Furthermore, there is a dependence also on wave-length: the greater the wave-length of the primary radiation, the smaller is its percentage change, because the absolute value of the wave-length change *h*/*mc* contains only universal magnitudes; that is, it is not

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[4] Kallman and Mark, "Naturwissenschaften," 1925, Vol. 14, p. 297. This contains very fine pictures of the effect.

proportional to the wave-length. Efforts to confirm this effect have been undertaken along two different lines. On the one hand, evidence was adduced (Ross) that visible light is not measurably changed during dispersion. On the other hand, it was shown (Compton) that $\delta\lambda$ remains constant with increasing X-ray wave-lengths. The following Figure 56 depicts the theoretical dependence upon angle of dispersion (continuous line) and the various $\delta\lambda$ values determined experimentally for different primary wave-lengths.

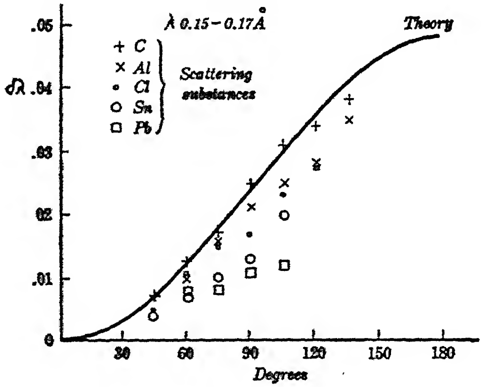

Fig. 56.

Moreover, it has been assumed in these calculations that only one electron—one loosely bound—takes up this recoil. This is without a doubt not always true. The very existence of the undisplaced line in the dispersion spectrum indicates that dispersion takes place without an attending change in wave-length, therefore, without a cleavage of energy from the primary light quantum. We may conceive such action by assuming that the entire atom, and not only the electron, experiences the recoil. Calculation shows that the mean $\delta\lambda$ is so much the smaller the greater the mass m that takes up the recoil. It may be expected, furthermore, that the pure Compton dispersion—as this dispersion with attending division of the primary quantum is termed—occurs the more rarely, the greater the number of electrons in the dispersing atoms. This is a modern interpretation of a result, long known, viz.: that the dispersed radiation is less "softened" in contrast to the primary radiation the higher the atomic number of the dispersing element. Since absorption analysis of the total dispersed radiation makes available conclusions only regarding the mean wave-lengths of the radiation, it will follow from such experiments that the mean Compton displacement computed from them will be the smaller the greater the atomic number. Figure 57 shows the results of such experiments by Compton. Here the dispersion of the K-radiation of tungsten by various substances under different angles of dispersion is plotted as abscissæ against the mean wave-length variations computed from the variations in the absorbability of the dispersed radiation, as ordinates. The continuous curve shows the δλ values as computed from the quantum theory in Ångstrom units. P. A. Ross has investigated directly by spectral means the dispersion produced by materials of widely different atomic number (Al, Cu, Zn, Ag, Pb) and has found that the intensity of the displaced line relative to that of the undisplaced line decreases markedly with increasing atomic number, but δλ itself remains constant. In investigating the total dispersed radiation a smaller mean δλ must result, the more the intensity of the displaced component recedes toward the undisplaced component, as is

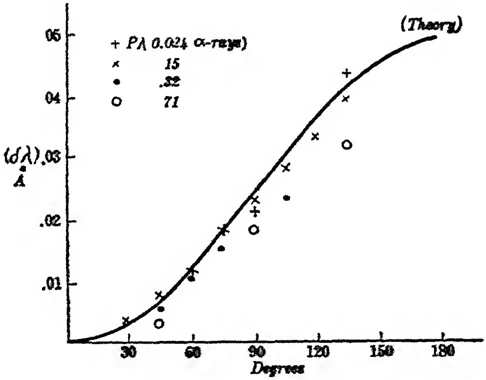

FIG. 57.

evident from Figure 57. It is evident that the variations in wave-length $\delta\lambda$ as computed from absorption analysis of dispersed radiation approximate the quantum theoretical values the more closely the smaller the atomic number of the dispersing substance.

However, the circle of evidence is not yet complete: W. Bothe[5] succeeded in giving evidence of the existence of the "recoil-electrons": electrons whose velocity is extremely small and which produce little ionization in gases. Ionization of gases by means of Roentgen rays is a secondary effect due to the separation of electrons from gaseous molecules, in other words, by means of a "photo-effect." The primary liberated electron in its passage through the gas ionizes the molecules struck by it. The velocity of these released electrons is generally large and may be calculated from the quantum relation for excitation by electron impact: a quantum $h\nu$ releases an electron and imparts to it the energy $\epsilon V = h\nu$. The total radiation energy is transferred to the electron. Usually the entire amount of the quantum does not appear as kinetic energy, which would be equal to the kinetic energy of the electron exciting the Roentgen radiation, since a portion of it is consumed by the work necessary to liberate it from the atom. Bothe has shown, also, that a large number of very slowly moving electrons are liberated in addition to these fast or rapidly moving electrons. These electrons move so slowly that they ionize gaseous molecules to a very small extent only. They are the "recoil electrons" whose value, theoretically, must be small since it is only the recoil energy that is imparted to them, viz.: the energy $h\partial\nu$ and not $h\nu$, where $\partial\nu$ is the frequency change in Compton's dispersion.

One more point: the Compton dispersion must not be confused with the reflexion of Roentgen rays from crystals, which constitutes the fundamental method of measuring the wave-lengths of Roentgen rays. There is question here not of individual and mutually independent processes, but rather of an effect of superposition of a great number of coherent

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[5] W. Bothe, Zeitschr. f. Phys. 16, 319 (1923), 20, 237 (1923).

waves. Here again undulatory optics, so foreign to the quantum theory, intervene with its fundamental interference phenomena. Naturally, a Compton radiation is likewise emitted by the spectrometer crystal, but this is so weak that it can barely be observed, even approximately, in such measurements. Kuhlenkampff has proven in a very beautiful and direct experiment that no change in wave-length arises in Bragg's selective reflexion from crystals. Compton dispersion and crystal-reflexion stand in the same relation to one another as the optical resonance radiation of rarified gases to the reflexion from dense metallic vapors, as was discovered by Wood and investigated thoroughly by Franck.

The one point which appears not to be definitely explained at this time is the very pronounced spectral width of the displaced frequency. And yet this is not unexplainable: in the first place, it is not possible just now to observe only that radiation which suffers dispersion exactly at a definite angle. But as soon as we have an angle-range, the "Compton line" will be broadened because of the dependence of the extent of displacement on the dispersion angle. And secondly, a sharp frequency always presumes that the recoil is taken up only by one electron—a free electron. The disperse electron, however, belongs to an atomic grouping; if the recoil is imparted to two or more of these—to equal or unequal parts according to the electron configuration in the atom—each will bring about a different displaced Compton line, or, on the average, will lead to an ill-defined line. It is indisputable that a further development of the experiment will lead to a revelation of new facts. Duane's observation that the Compton line is more intensive in short wave-primary radiation (tungsten) than in long wave radiation (molybdenum) already presents new problems.

The Compton Effect more than all other quantum phenomena necessitates the assumption of light quanta and their directed emission, thereby extending on the one hand our knowledge of the mechanical behavior of the quanta, on the other hand widening the rift between the quantum theory of emission and absorption and the wave theory of light propagation.

This rift has been made more pronounced within the last years by proving as extremely certain the atomistic-mechanistic character of the Compton Effect. We will first discuss the direction of the recoil electrons relative to the vibration direction of the electrical vector of the Roentgen ray.[6] If an electron is liberated because of the absorption of a Roentgen ray quantum and if it assumes the entire Roentgen quantum energy, such an electron (for brevity, termed the "photo-electron") will continue preferably in the direction of the atom in which the electric vector of the Roentgen ray is vibrating. If, therefore, a Roentgen photo-effect is produced by means of polarized Roentgen light, the direction of the expelled photo-electrons will lie in the plane of the Roentgen ray vibration[7] (see Fig. 58). If, however, the Roentgen ray experiences a "Compton dispersion," the "Compton recoil electron" cannot give evidence of this direction. On the contrary, its direction must be perpendicular to the vibration direction of the dispersed Roentgen ray (Fig. 59). For under these conditions, the electron is expelled not as the result of the vibration effect of the absorbed quantum, as in the photo-effect, but rather because of the mechanical recoil of the emitted secondary Roentgen ray quantum. The proof of this phenomenon is due to F. Kirchner.

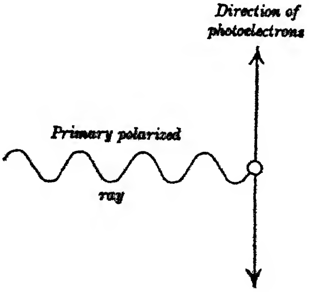

FIG. 58.

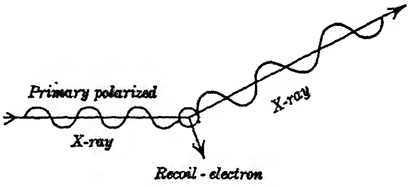

FIG. 59.

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[6] F. Kirchner, Physik. Zeitschr. 27, 385 (1926).

[7] F. W. Bubb, Phys. Rev. 23, 137 (1924).

A. H. Compton and A. W. Simon have performed other experiments on the direction of these electrons. They endeavored to establish that the direction, as demanded by theory, between the paths of the recoil electron and of the dispersed Roentgen ray quantum actually is obtained; even more, they wish to determine whether we can speak of a direction of the dispersed quantum in the sense of the quantum theory of light. In these investigations they employ Wilson's condensation method which was utilized also by Kirchner in the previously described experiment. This method is based upon the fact that fog droplets will condense the more readily in an atmosphere supersaturated with water vapor wherever there may be ions. It is possible likewise—as was done by Bothe in the work mentioned above—to detect the appearance and the path of a recoil electron by noting the sudden appearance of a series of minute fog droplets. Let point *A* in Figure 60 designate the head of such a chain of droplets. Roentgen rays themselves are not detectable by this condensation method, although we may detect the existence of a Roentgen ray which is not dispersed but which is emitting a photo-electron. This photo-electron will induce ionization, thus bringing about condensation of water vapor; the beginning of the series of droplets will indicate the position at which the Roentgen ray was absorbed. If this position *B* is connected with the head *A* of the path of the recoil electron, a definite angle will be formed between this direction line *BA* and the direction of the recoil electron *AE*. This angle shows the dependence on the disperse angle as demanded by Compton's theory. Naturally this result is obtained only as the mean of very many individual experiments. It may be emphasized, in this connection, that few experiments are capable of showing it; for

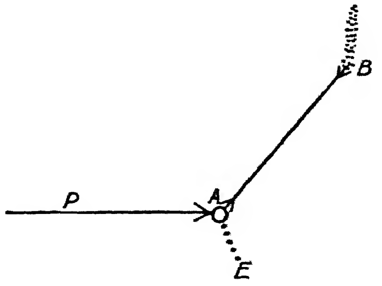

FIG. 60.

a satisfactory result many favorable conditions must be operative simultaneously. Thus, it is necessary, in the first place, that the dispersed Roentgen ray following its dispersion expel a photo-electron before experiencing a second dispersion. Secondly, the dispersed Roentgen ray must have experienced likewise a Compton dispersion, i.e., it must have emitted a recoil electron; and finally, the respective paths of the recoil electron and the photo-electron must be of such intensity that their starting points can be observed directly. The experimental arrangement therefore is not very simple, since a large number of individual actions occur simultaneously, that is, many electronic paths will be traced upon a photographic plate. Thus, of 850 exposed plates only 38 showed signs of recoil and photo-electrons, and of these 38, only 18 gave traces conforming to the theoretical dependence upon angle. This per cent is so high, however, that it surely cannot be explained as due to mere chance. In addition this experiment furnishes evidence that the dispersed Roentgen ray may be conceived as a directed quantum in the sense of the extreme light quantum hypothesis.

The question whether dispersion of the Roentgen rays and expulsion of the recoil electron occur simultaneously (as is required on the simple mechanical explanation of the Compton Effect) has been answered by W. Bothe and H. Geiger. These investigators employed the so-called Geiger "counting chamber" to detect the electron and the dispersed Roentgen ray. This method is based upon the observation that a discharge proceeds from a point connected with a pole of a source of high potential. A discharge may well take place in a gas even though the applied potential lies below the normal discharge potential provided there are present sufficient carriers of electricity. When these approach closely to the point, they are so strongly accelerated that they produce sufficient ions in the gas by impact ionization to generate a discharge. This discharge will discontinue immediately as soon as the ions are used up, i.e., the point discharge will take place intermittingly as the ions are alternately accumulated and consumed. Geiger counting chambers thus measure not only the recoil electrons but the Roentgen rays as well, because the latter expel electrons at the point itself. Geiger and Bothe place two such counting chambers opposite one another and introduce between them the gas in which Roentgen rays are dispersed (Fig. 61); observations are made by noting whether the discharges of the Roentgen ray counter [8] (*hν* counter) coincide with the discharges of the electron counter; they observe such a large number of coincidences in both processes that sufficient evidence is established to show that dispersion of the Roentgen ray quantum and recoil of an electron proceed simultaneously.

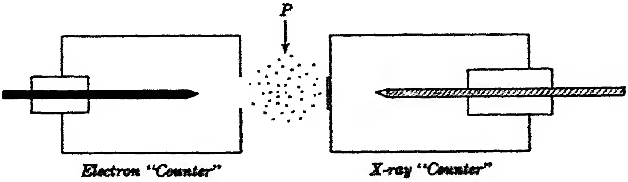

FIG. 61.

The only conclusion that may be deduced from all these experiments is: the emission of the dispersed Roentgen ray consists in the directed emission of an energy quantum $h\nu$ with the impulse $h\nu/c$. Thus considered, they constitute the proof for all the assumptions in the theory of Compton dispersion.

Although the quantum theory of light seems to be confirmed by these experiments, other experiments by H. Mark and H. Kallman [9] on the properties of Compton dispersion indicate that the classic wave character of this radiation is likewise experimentally demonstrable. Thus they find that Compton's disperse radiation is polarized linearly as would be anticipated on the basis of the classical theory of dispersion; and furthermore, the vibration state of the Compton radiation depends unequivocally upon the vibration condition of the primary radiation.

[8] This is protected against penetration by electrons by means of a foil.

[9] H. Mark and H. Kallman, "Die Naturwissenschaften," 1926.

It is thus apparent that the classical theory and the quantum theory are more strongly opposed than ever before.

In connection with this problem as to the nature of Roentgen radiation we will comment briefly upon some very interesting work carried out recently by Joffe and Dobronrawow.[10] It was shown by them that a bismuth particle of about 10^{-5} cm. diameter which could be suspended for hours in a Millikan condenser while positively charged, loses a photoelectric electron very rarely when illuminated with Roentgen rays. The Roentgen tube furnished Roentgen impulses in the time interval of 10^{-3} seconds. The particle was observed from the anticathode at a space angle of 10^{-5} to 10^{-6}. Only every 30 minutes, on the average, were electrons released by the bismuth particle, while in the same interval about 10^6 Roentgen ray impulses passed by it. Since we must exclude the possibility that the particle very slowly accumulates from the 10^6 impulses during the 30-minute interval the energy requisite for the emission of electrons, we can only assume that the energy of an impulse is concentrated within a definite angular space, which is smaller than 10^{-5}. The experiment, therefore, favors the extreme light quantum theory and indicates the existence of a "needle radiation."

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[10] Joffe and Dobronrawow, Zeitschr. für Phys. 32 (1925).

CHAPTER XVIII

THE EXTENSION OF OUR KNOWLEDGE OF THE ELECTROMAGNETIC SPECTRA

Investigation of the electromagnetic spectrum had its inception, as is known, in the study of "optical spectra," the region of waves that fall within the visibility, i.e., the sensitivity of the eye. Physical examination of these waves with objective methods (by measuring the radiant energy or by photographic fixation) revealed the presence in them of other emissions beyond the red and violet limits of the visible spectrum, designated according to their position as infra-red (Herschel, 1800) and ultra-violet (Ritter, 1801). Their investigation was continued with the usual optical methods by dispersing the total emission by means of prisms and diffraction gratings. These investigations were limited in range because of absorption in the materials of the optical apparatus employed. In addition there was developed the region of electric waves, a region sought for and eventually discovered by H. Hertz on theoretical considerations. This was followed soon by the knowledge of the similarity in nature of the electric waves and optical waves. Whereas the wave-lengths of the latter were of the order 1/1,000 mm., the former were characterized by longer wave-lengths ranging in length from centimeters to meters and even to kilometers. The region of intermediate wave-lengths was first explored and disclosed by H. Reubens, so that there are practically no more gaps in the scale of wave-lengths between the ordinary "optical" waves and the "electric" waves. Succeeding investigations of Roentgen rays beyond the short waved end of the visible spectrum showed plainly that this radiation is similar in character and general properties to the optical and electric waves because of similarity in polarization and interference phenomena. Adjoining these waves is a region of still smaller wave-lengths, the so-called γ-rays. Until recently a gap still remained between the visible spectrum and the region of the Roentgen radiation. This was bridged over, however, by the simultaneous extension of the optical spectrum to shorter waves and of the Roentgen spectrum to longer waves.

The following table is a résumé of the regions explored to date.

	Wave-lengths in c.cm.	Explored with
Waves of wireless telegraphy............	$> 10^4$	
Shortest electric waves....	10^2–10^{-1}	Grating. Prism-energy measurements. Interferometer. Excitation of elect. vibrations.
Infra-red Hg-vapor emission..............	3×10^{-2}	Grating Interferometer } Energy measurements.
"Rest" region...........	1.5×10^{-2}-2×10^{-3}	
Short wave infra-red......	2×10^{-3}-8×10^{-5}	Grating, energy measurements. Prism, 10^{-4} photography.
Visible light............	8×10^{-5}-4×10^{-5}	Photography.
Ultra-violet...........	4×10^{-5}-1.8×10^{-5}	Prism { Ionization.
Schumann region.........	1.8×10^{-5}-1.2×10^{-5}	Photoeffect.
Lyman-Millikan region....	1.2×10^{-5}-1.5×10^{-6}	Grating, photography.
Long wave Roentgen rays.	7.0×10^{-6}-2.0×10^{-7}	Quantum calculation from excit. energy. Ionization.
Roentgen rays...........	2.0×10^{-7}-1×10^{-9}	Crystal grating Energy Meas. Crystal grating Photography.
Gamma rays............	$< 10^{-9}$	Absorption analysis Ionization.

The wave-lengths from the infra-red region down are measured in μ, $\mu\mu$, or Å. (Ångstrom units). These units are related as follows: 1 cm. = 10 mm. = $10^4 \mu$ = $10^7 \mu\mu$ = 10^8 Å. The vibration numbers are obtained from the relationship $c = \nu\lambda$ (vibration number × wave-lengths). Frequent use is made in spectroscopy of the "wave number" instead of the frequency, or vibration number. This is the number of waves per cm., i.e., the wave number $n = 1/\lambda = \nu/c$; the dimensions are, therefore, sec.^{-1}, n cm.^{-1}.

The individual regions listed in the table have been selected in the usual manner which rests partly upon the method of measurement. In reference to regularities to be discussed elsewhere, we may mention here that "Millikan's region" partly overlaps with the "long wave Roentgen rays" because the same characteristic atom frequencies were excited, identified and measured by two different methods.

The same applies to the region lying between the infra-red and the short electric waves as is indicated by the recent investigations of Nichols and Tear.

The prime physical significance of the exploration of this region of electromagnetic waves is not so much the knowledge of their existence. It lies rather in the utilization of these vibrations as an aid to the exposition of the basic problem of physics, the problem of the structure and the essence of matter into which the older problem of the radiation mechanism has merged completely. Experimentation along this direction has already borne the richest fruit. The original radiation problem, on the contrary, the question regarding the essence of light, is today more than ever shrouded in darkness. Thus, the knowledge of the atomistic emission of radiation and the atomistic effects of radiation, on the one hand—constituting a considerable portion of the quantum theory, so well founded in experiment—are diametrically opposed to the regularities of the diffusion of radiation—the classic wave theory and its apparently unequivocal confirmation by interference and polarization phenomena—on the other hand.

We will now cursorily review the knowledge obtained by the utilization of radiation of various frequencies that bears on the problem of the nature of matter as far as this problem is atomistic in scope. In this first place, we may consider crystal structure. The discovery of the infra-red "rest rays" by Rubens prompted E. Madelung to propose the theory of crystal structure according to which crystals are constituted of electrically positive and negative ions. Frequencies selectively reflected metallically by crystals in the infra-red were designated by Rubens "rest rays" of the substance. Thus, while rock salt is always strongly transparent to the short wave infra-red, it reflects metallically in the region 50–53 μ, and thus it becomes possible to isolate this spectral region by reflecting a continuous spectrum on rock salt plates. Correspondingly similar reflection regions were determined for many other crystals. These may be conceived as the resonance of the possible frequencies in the solid crystal depending upon the charge, the magnitude and the type of ions within it. The nature of the elemental constituents (building bricks) forming the crystal was thus established. The lattice theory of crystal structure became more firmly intrenched by means of the Roentgen rays and the demonstration of interference phenomena by Laue, Friedrich and Knipping; and finally, by adopting another method utilizing the shortest wave-lengths, the ionic charge of the structural units of the crystal (as determined from the behavior of the crystals toward radiation of long waves) was confirmed by Debye and Scherrer. Experiments attempting to explain, by means of electric waves, the characteristic properties of liquids and gases do not seem less successful; for example, the determination of natural electrical moments in the molecules. For the same end knowledge of the dispersion process of the same substances in the visible and ultra-violet regions is necessary. The infra-red rays may likewise serve the same purpose by determining the characteristic absorptions, especially in gases, whereby those rays are absorbed that correspond to the specific vibrations of the molecules—monatomic gases and vapors have no infra-red "molecular" absorption.

But far more important was the determination of the existence of a characteristic radiation of long wave-length of illuminated mercury vapor which ordinarily is ascribed to molecules. (Incidentally, we may remark that this is the longest infra-red radiation measured thus far.) The presence of such a wave-length indicates that monatomic gases in and by themselves can form polyatomic molecules under certain circumstances, whose existence may be verified, in turn, by optical vibrations in the "band spectra." Conclusions may be drawn regarding the form of the gaseous or vaporous atoms and molecules from the depolarization phenomena of the light dispersed by them, the so-called Tyndall cone, whose appearance in very pure gases recently has been confirmed by Gans and Baron Strutt (Lord Rayleigh). In addition, we may mention here the determination of the absorption frequencies of normal atoms and of atoms and molecules excited electrically or thermally, which have influenced, in conjunction with the investigations on the excitation and emission of spectral line and the quantum considerations, our present conception of the atom (and atomic structure). The electrons in an atom may be counted by measuring the scattering of the X-rays, and the rays inform us regarding the disintegration of the atomic nucleus.

Many of these problems are discussed elsewhere. We will turn our attention to the consideration of those frequency regions that have been extensively investigated most recently.

Infra-red Spectrum

We shall begin our consideration of the infra-red spectrum with investigations undertaken during the last decade on the long wave infra-red region, which has been explored rather methodically by H. Rubens. But, whereas the methods available in the past permitted only indirect measurement of the wave-lengths of these emissions, Rubens recently has carried out their absolute measurement in grating refraction spectra and thus strongly confirmed the correctness of his former conclusions. His grating measurements extend to 325 μ, that is, to 0.3 mm., so that at present the regions 3×10^6 to 1.5×10^2 Å. have been explored and measured, the former by means of refraction gratings, the latter by means of crystal gratings.

We shall consider two points with reference to the methods of infra-red investigations: the detection of long wave radiation, and the production and isolation of long wave radiation from emissions of any radiating source and their spectral dispersion.

Wave-lengths of about 1 μ and upwards are not directly "fixable" photographically; even "red-sensitization" ("rotsensibilisierung") fails. On the other hand, it is quite possible, by concentrating long wave radiation upon photographic plates, to induce a "developable" change in the silver bromide of the plate as a consequence of the heat generated by the absorption of the radiation. Langley seemed to have obtained such a "photograph" in one of his experiments, although others failed to obtain a similar effect. The heat effect, referred to, may be rendered serviceable to infra-red photography in the method of phosphorescence photography. A substance (e.g., Lenard's phosphorus and the familiar "Sidot blendes" stimulated to phosphorescence by a previous exposure to ultra-violet radiation) will re-emit, according to Lenard's law of the constancy of light, until the product of the radiated energy into the period of radiation equals the light quantity (energy) absorbed during stimulation. The velocity of the re-emission may be varied by change in temperatures, the re-emission being accelerated with rise in temperature. If, therefore, infra-red radiation be focussed upon one portion of a phosphorescent screen for some time, the spot so affected will lose its phosphorescent character after a certain interval, that is, the phosphorescent plate will have become dark at the spots exposed to the infra-red radiation. If such a screen be placed upon the active side of an ordinary dry plate, the latter will be darkened, excepting that portion of it placed opposite to the "dark" spot of the phosphorescent screen. In other words, we obtain a "positive" of the infra-red radiation. The following Figure 62 presents such a phosphorescence photograph due to A. Ignatieff: an interferometer photograph of the 1 μ helium line by means of a Perot-Fabry plate.[1]

FIG. 62.

A similar method was elaborated by Terenin; he utilized for the photographic fixation of infra-red radiation the "cloudiness" formed on a plate by preliminary exposure.[2]

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[1] Ann. der Phys. 43 (1914).

[2] Zeitschr. f. Phys. 23, 294 (1924).

Although this method is serviceable per se and applicable to long waves generally, its use is prohibited in such cases where the energy of the rays no longer suffices for very long waves to obtain a noticeably more rapid phosphorescence of the illuminated parts as opposed to the unilluminated parts. True, systematic experimentation along these lines has not yet been attempted; for example, the investigation as to whether a more pronounced sensitivity could not be procured at lower temperatures of the phosphorescing substance. Up to the present time, thermal effects of the absorbed rays were used directly for the detection and measurement of their intensity, the apparatus commonly utilized being the thermopile, bolometer, microradiometer and radiometer. Research was particularly necessary to obtain a suitable "blackening material" for the illumined portion of the receiver, since lampblack and platinum black no longer were satisfactory because they are transparent to the long waved heat rays. Mixtures of lampblack and sodium water glass spread upon the receiving plate were found especially suitable, a high (about 95 per cent) absorption capacity equally suitable for all wave-lengths being obtained.

To date, three methods have been employed to produce thermal rays of long wave-length: solid radiators (black bodies) of high temperature, whose radiation intensity for long waves is proportional to the absolute temperature (see chapter on radiation measurements), Welsbach burners, which (from very uncertain reasons—band spectra of oxides?) are characterized by a particularly strong emission of long wave-length, and thirdly, the high pressure-quartz-mercury vapor lamp with its moderately monochromatic emission and very long waves (see below).

The following methods serve for the isolation of these waves:

1. The filter methods.
2. The method of "rest rays."
3. The method of polarized "rest rays."
4. Diffraction gratings.
5. Quartz lens methods.

Typical normal filter methods in the infra-red are amongst others: Paschen's filter for 1 μ (for detail, see below) and the use of "Biotit" or molybdenite (and several similar minerals). These absorb all rays except a certain infra-red range to which they are transparent. Due to a deficiency, however, of such filters, another procedure is most frequently adopted. There are many substances, usually crystals, which exhibit a marked absorption in a limited spectral range. Rubens has elaborated the following method to examine such a spectral range—let us say, to study the extent of its absorption in other substances. In this method the "absorbing" crystal is utilized as a "screen." If it is placed in the path of the radiation, all wave-lengths will pass through it excepting the spectral region under investigation (its selective absorption range). The transmitted radiation serves as a "zero" or "null point." Upon withdrawal of the crystal the previously intercepted range will now be added to the "zero radiation."[1] Of course, a very fine spectral dispersion is not obtained. Nevertheless, the method serves frequently to great advantage, as indicated by the data of Rubens.

Since the extent of the transparency depends upon the thickness of the "filter" medium, the (variation) possibility for narrowing or confining certain wave-length regions is decidedly increased.

It will not be amiss to list here the numerical data on the transparency of a few materials that find optical application.

Good glass (glass that is clear and not green in thick layers) of 5 mm. thickness is transparent to radiation of 1 μ to the extent of 70 per cent and for radiation of 2 μ from 40–50 per cent. For radiations above 4.5 μ glass of 1 mm. thickness is opaque for all practical purposes. Thicknesses of 0.1 mm. allow the passage of radiation up to 23.7 μ to the extent of a few parts per thousand. Its reflective capacity for 23.7 μ is 19.7 per cent, from which we may calculate, by means of Fresnel's equations, its index of refraction. This is

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[1] For a modification of this method for compensating the reflexion-loss by the crystal, see M. Czerny, Diss. (Berlin, 1922).

found to be 2.55 (for visible light it is about 1.6). Glass is entirely opaque to wave-lengths λ equal to 51.2 and 61 (D is smaller than 0.05 per cent). The calculated index of refraction for $\lambda = 51.2\ \mu$ on the basis of a reflection capacity r of 15.7 per cent is 2.3, and the corresponding value for $\lambda = 61$, whose $r = 11.3$ per cent, is 2.0.

Quartz commences to absorb very strongly at wave-lengths of 6 μ. For 23.7 μ, its transparency at 2 mm. thickness is 0, and for 0.03 thicknesses about 15 per cent. The corresponding reflectivity r is 41.7 per cent, from which the index of refraction n may be calculated, as above, to be equal to 4.62. For long waves quartz again becomes transparent.

	$\lambda = 51.2$	$\lambda = 61$
D for 0.5 mm. thickness	61%	77%
D for 5.25 mm. thickness	8%	18%
D for Reflectivity	17.8%	13.0%
n	2.48%	2.14%

Data for longer waves perpendicular to the optical axis of quartz crystal:

λ	D (for 1.93 mm. thick)	D (for 3.99 mm.)
51 μ	20%	9.5%
60 μ	37.5%	18%
80 μ	50%	32%
100 μ	65%	52%
110 μ	68%	60%

Mica is transparent to $\lambda = 23.7\ \mu$ as shown in the table:

For thickness 0.015 mm.	9.9%
For thickness 0.032 mm.	8.3%

Its reflectivity is 28.7 per cent, from which n is calculated to be 3.32.

For thickness of 0.02 mm. we have the following:

λ 51.2 μ	D = 53%	Reflectivity = 13.4%	$n = 2.15$
λ 61 μ	D = 55%		

Fluorite is readily transparent up to 7 μ. For wave-lengths 23.7 (rest rays of fluorite) it reflects to the extent of

71.5 per cent. For longer waves of a thickness of 5.6 mm. we have

51.2 D = 4% Reflectivity = 31.0% $n = 3.5$
61 D = 6% Reflectivity = 20.4% $n = 2.65$

Sodium chloride (rock salt) in layers 1 centimeter thick is transparent to about 90 per cent to wave-lengths 9 μ, and absorbs almost perfectly for values above 20 μ. Measurements for 23.7 μ are as follows:

Thickness 1.92 mm. D = 11% Reflectivity = 1.7% $n = 1.22$
Thickness 2.1 mm. D = 2.1%
Thickness 14.0 mm. D = 0.02%

Filters recommended for radiation of 1 μ and 2 μ are the following: 1 μ, filters of F. Paschen[4] composed of Wratten-Wainwright filters FN = 28 (or 29), HN = 45 (or 44) and a 1 cm. water layer, isolates the helium line 1.08 μ to the extent of 69.3 per cent, the cadmium line 1.04 μ to the extent of 69.5 per cent, the zinc line 1.10 μ to the extent of 62.5 per cent, and transmits the adjacent line 1.3 μ only to the extent of 18 per cent. Wood's infra-red filter is considerably less transparent and monochromatic than Paschen's filter.

For 2 μ radiation, A. Ignatieff recommends (according to Königsberger's process) green biotite (iron-magnesia mica) 0.11 mm. thick, which absorbs 1 μ almost completely, but is transparent to 2 μ to extent of 70 per cent; the filter, however, is likewise transparent to radiation of longer wave-lengths.

The second method of isolating definite radiations, the method of "rest rays," is superior to the method just described, because the reflection ranges are spectrally "sharper" than are the absorption ranges. The usual method of procedure is evident from the following Figure 63; data on the "rest rays" measured thus far are listed in the table below. More shall be said later regarding the direct measurement of wave-lengths by means of diffraction gratings—which were first determined interferometrically by means of quartz interferometers. *L* is the radiation source. The radiation

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[4] F. Paschen, Ann. d. Physik 43, 859 (1914).

is rendered parallel by reflection from a concave mirror (silvered surface) and then reflected successively from the plates P_1, P_2, P_3 of the substance under investigation. After this threefold reflection, the normally reflected radiation—non-metallic reflection—has become so weakened that the mirror S_2 will focus upon the measuring devise *Th* only the "rest rays," that is, the "metallically reflected" wave-lengths. Large crystal plates are necessary to procure sufficient energy; in the case of sodium chloride these are readily available (a rough polish is sufficient). It was not possible, however, to obtain crystal plates of several square centimeters surface from substances like thallium iodide. Rubens, accordingly, utilized a powder compressed under high pressure in a metallic mold, whose surface was "polished" by the attrition of two such preparations over one another. Or—whenever possible—he constructed "mosaics" from smaller crystals which subsequently were planed and burnished. The "polish" given these preparations may vary, being the coarser the greater the wave-length of the "rest rays"—dispersion of radiation of very long wave-length due to the coarseness of the surface no longer is considered.

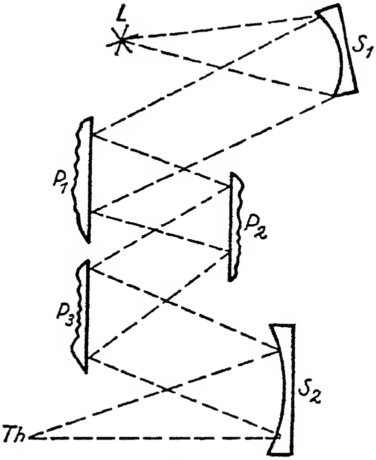

FIG. 63.

Notwithstanding these simplifying possibilities it was desirable to possess a method which would utilize but one plate of the substance under investigation. Such a procedure—based upon a suggestion of H. Rubens—has been elaborated by M. Czerny. This procedure is termed the "method of polarized rest rays." There are two varieties, one of which will be discussed here.

TABLE

	Wave-lengths in μ			Remarks
Gypsum				
Quartz	8.50	9.02	20.75	
Mica	9.20	18.40	21.25	
Fluorspar	24.0(?)	31.6	—	
Rock salt	52	—	—	Increases with greater atomic weight of positive ion in crystal.
Sylvite	63.4	—	—	
Silver chloride	81.5	—	—	
Potassium bromide	82.6	—	—	
Thallous chloride	91.6	—	—	
Potassium iodide	94.1	—	—	
Silver bromide	112.7	—	—	
Thallous bromide	117.0	—	—	Increases with increasing atomic weight of the negative ion in the crystal: Tl with Cl, Br, I.
Thallous iodide	151.8	—	—	

In Rubens' "rest ray" method a multiple reflection, that is, reflection from successive plates, is necessary to acquire a satisfactory spectral purity. If it is desired to isolate radiations of very long wave-lengths from a given radiation source, it must be recalled that but an extraordinarily small portion of long wave rays is present in the total spectrum of every "radiator"; by far the greatest portion of these rays, at temperatures of the radiator, lies somewhat between 0.8 μ and 10 μ. The energy decreases with increasing wave-length, proportional to λ^{-4}. To isolate, as much as possible, only monochromatic "rest rays," it is necessary that the reflection capacity of the short wave rays be very small. Czerny's method is based upon the laws governing the reflection of polarized radiation. According to Fresnel's formula a given radiation, whose electric vector lies in the plane of incidence, no longer is reflected below a fixed angle, the so-called "polarization angle." If, however, the reflecting substance exhibits for certain wave-length ranges the phenomenon of "rest ray" reflection, i.e., if it exhibits for these wave-lengths "metallic characteristics," Fresnel's law no longer will apply, at least as regards this range, for the polarized radiation of this wave-length will now likewise be reflected. There is thus developed, on the basis of this simple consideration, a new method to obtain spectrally pure "rest rays" by reflection from a single plate. The light from the radiation source is first polarized linearly by reflection on a selenium mirror and is then incident, below the polarization angle, upon the "rest ray" plate in such manner that its electric vector falls in the plane of incidence. Under such conditions, short and long wave radiations will not be reflected at all with the exception of the wave-length range in which the crystal plate reflects "metallically." In this wise, reflection from one plate makes possible the filtration or isolation of "rest rays."

The diffraction grating method (fourth method of radiation filtration) differs in no way from the spectral dispersion of other spectral regions by means of gratings. More will be said in a later section regarding the use of the wire gratings in the long wave infra-red regions. For very precise and accurate measurements in the short wave regions of the infrared the so-called "Echelette" gratings (Trowbridge) have been used extensively in America. These are standard gratings (gold-plated copper surfaces) so ruled as to give a definite form to the grating grooves which are so chosen that the greater part of the energy in a limited region is reflected, e.g., of a given wave-length range of a definite order. The increase in energy gained together with the greater dispersion power of these gratings has made possible a number of measurements of extreme accuracy in the short wave infra-red band spectra (water, carbon dioxide, hydrogen chloride, etc., in the region $2\ \mu$–$6\ \mu$).

Finally, there is the quartz lens method of Rubens and Wood. This is founded upon the very high index of refraction of quartz beyond its absorption range in the infra-red, that is, for waves of wave-length of $100\ \mu$ or more. Consider Figure 64.

S is the substance emitting long wave infra-red radiation. L_1 and L_2 are two large quartz lenses taken as thin as possible whose focal lengths for long waves (index of refraction being about 2.14) is 10 cm. Lens L_1 projects an infra-red image of the radiation source S at B_1; the short wave rays, corresponding to their smaller index of refraction, are more divergent (their boundary being indicated by the broken lines). The screen about B_1 intercepts these rays. By means of a second lens L_2, similar to L_1, B_1 is focussed upon a measuring device (e.g., a thermopyle). In order to intercept also the short wave radiations (the middle ray) which are transmitted through the lens directly from S, small circular paper discs are pasted centrally upon the lenses. This arrangement makes available long wave radiation of more than (ca.) 80 μ.

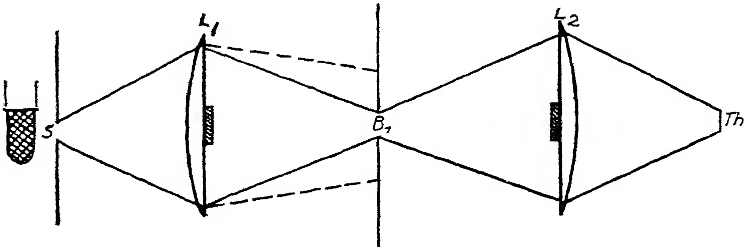

FIG. 64.

Measurements in the infra-red region are of importance to the solution of widely different problems, e.g., the discovery of substances that exhibit "rest rays" and the determination of the wave-lengths of these regions of selective metallic reflection so as to explain the nature of the crystal forces; the investigation of selective emissions, that is, to extend and supplement measurements on line and band spectra similar to those in optical regions (problems of atomic and molecular structure); the determination of the absorption regions of solid, liquid and vaporous bodies, and the exact measurement of the fine structure of absorption spectra (problems of molecular structure); the examination and testing of conclusions derived from Maxwell's electromagnetic theory.

The results of the investigations on "rest rays" in the long wave [5] infra-red are due almost entirely to the work of

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[5] For reflexion in short wave infra-red, see Chapter XXII.

H. Rubens and his coworkers. These data are summarized in the table below in which the reflection ranges in μ are given for a number of substances.

The longest radiation measured was contained in the emission of the mercury-quartz lamp. Its wave-length lies in the neighborhood of $300\ \mu$ (about 1/3 mm.). We shall discuss the exact measurement of the wave-lengths by means of diffraction gratings in a later section. This long wave radiation makes it feasible for us to test a relationship of the electromagnetic theory of light. The reflectivity R and index of refractions n of a given substance are related according to the expression

$$R = 100 \frac{(n-1)^2}{(n+1)^2}.$$

Substance	R Observed for $300\ \mu$	Dielectric Constant	R Calculated
Calcite	25.0	8.3	23.5
Marble	24.5	8.2	23.3
Gypsum	22.1	7.5	21.6
Fluorspar	19.9	6.82	19.9
Rock salt	17.9	5.82	17.2
Sylvite	14.0	4.75	13.8
Potassium bromide	14.9	4.66	13.5
Potassium iodide	15.8	5.10	14.9
Ammonium chloride	19.8	6.85	20.0
Ammonium bromide	21.1	6.98	20.3
Silver chloride	31.4	10.9	28.5
Silver bromide	35.6	12.1	30.7
Silver cyanide	17.3	5.57	16.4
Mercuric chloride	19.1	6.52	19.1
Mercurous chloride	33.5	9.36	25.7
Thallous chloride	56.7	35	51
Thallous bromide	59.7	42	54
Thallous iodide	50.3	30	47
Lead chloride	51.8	42	54
Water	15.1	81	64
Sulphuric acid	21.7	—	—
Glycerin	9.4	56.2	58
Castor oil	4.8	4.78	13.9

According to Maxwell the index of refraction is equal to the square root of the dielectric constant. This relation is valid only for long waves. These are available for use in optical investigations only in the long wave mercury radiation. Rubens has investigated their reflection from a large number of substances of known dielectric constants E. In the table p. 285, the reflectivities computed from the relation $\sqrt{E} = n$ are compared with the directly measured reflectivities for $\lambda \sim 300\ \mu$. Almost in every case we find agreement in observed and calculated values.

As stated above, wave-length measurements in the very long infra-red have been carried out recently by means of diffraction gratings.[6] Three copper wire gratings were used; their dimensions were: 8×8 cm. surface; wire diameters respectively 1.000, 0.483, and 0.196 mm.; space between wires (open meshing) was equal to the wire diameter in each case (i.e., the grating constant was equal to twice the wire diameter). Figure 65 shows the experimental arrangement. The radiation arising from the source A is reflected, by the way of the concave mirror H, the slit S_1, concave mirror H_1, grating G and concave mirror H_2, to the slit S_2 whose image is focussed by means of the quartz lens L upon the microradiometer M. To focus the various waves the spectrometer arm S_1H_1 and the rigidly attached parts S_1 HPA are turned. The central part of the quartz lens L is screened off by means of a small paper disc α. The focal length of the lens for visible light is 27 cm. But since the index of refraction of quartz for long waves is considerably larger (λ 110 μ, $n = 2.13$;

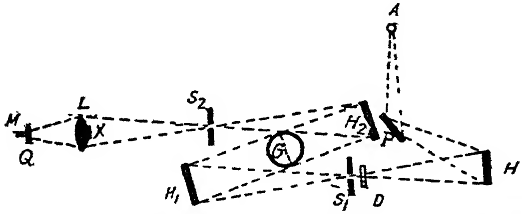

FIG. 65. A, Light source; HH_1H_2, concave mirrors; S_1S_2, slit; G, wire grating; D fluor-spar block; L, quartz lens; M, radiomicrometer; Q, filter plate.

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[6] H. Rubens, Berl. Ber. (21, 10, 1921), 1921, 8. Similar experiments by H. Witt (Physik. Zeitschr. 21, 874, 1920) appear to be influenced because of non-exclusion of the short wave radiation.

λ 313 μ, $n = 2.11$), the mean focal range for the spectral range under measurement is 13.0 cm. By means of the paper disc undiffracted or slightly diffracted radiation of short wavelength is prevented from passing through the middle of the lens and reaching the microradiometer. The introduction of the quartz lens (cut almost perpendicular to the optical axis) serves also an additional purpose. It is necessary that the radiation be entirely freed and purified from short wave radiations, since their intensity is overwhelmingly great in comparison to that of the long wave radiation to be measured. Furthermore, the radiation sources ordinarily utilized are extremely inconstant; temperature variations, however, will affect the long wave radiation but slightly, but not so the short wave radiation which is affected considerably. For this reason a transparent fluorspar block *D* is inserted as a "screen" to filter out the radiation on its way to the spectrometer. The fluorspar *D* is transparent to short wave radiation, permitting this to pass through it almost undiminished in intensity, while it absorbs the long wave radiation which consequently becomes accessible to the spectrometer only upon the withdrawal of the fluorspar screen. The quartz lens itself shows a high absorption power

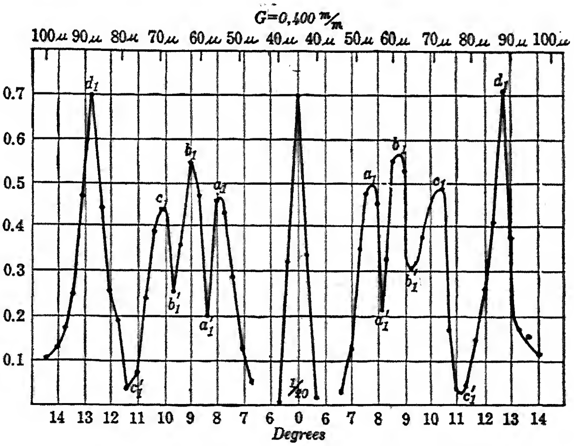

FIG. 66. Welsbach Burner, grating of large dispersion.

in the range 5 μ–50 μ; as a consequence only the following radiation arrives at the microradiometer: short wave infra-red and visible radiation, and upon removal of the fluorspar filter there is added infra-red of longer wave-length.

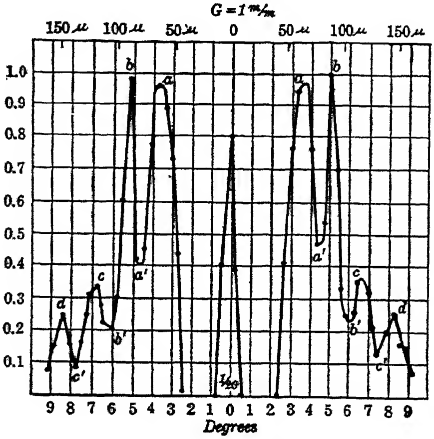

FIG. 67. Welsbach Burner, grating of small dispersion.

We will reproduce several of the diffraction spectra obtained (Figs. 66, 67 and accompanying table), e.g., the spectrum of a Welsbach burner obtained by means of two gratings, whose constants were, respectively, 0.400 and 1.00 mm. A more pronounced resolution is evident in the second case, where three maxima a_1, b_1, c_1 take the place of the single maximum *a* and d_1 corresponds to the maximum *b* of the previous figure. For a better orientation and understanding of the figures, the calculated wave-lengths are listed in the diagrams. The central curves at 0° represent the image of the slit drawn with greatly reduced ordinates (1/20). The wave-lengths are:

Maxima	λ (μ)	Minima	λ (μ)
a_1	54.6	a_1'	57.6
b_1	61.8	b_1'	65.9
c_1	70.6	c_1'	78.0
d_1	87.5	a'	78.1
b	87.1	b'	105.8
c	117.7	c'	132.2
d	144.8		

These wave-lengths are not the selective emission radiations of the Welsbach mantle but rather the selective absorptions of the continuous radiation of the Welsbach burner in the water vapor of the air. We will return to a discussion of these in a later section.

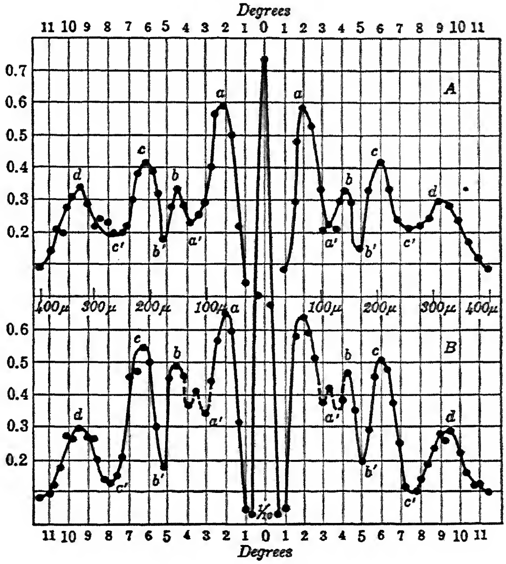

FIG. 68. Mercury-Quartz lamp.

A selective emission was observed in the long waved spectrum of mercury vapor. Figure 68 depicts this emission the wave-lengths of which are tabulated in the accompanying table.

Maxima	λ	Minima	λ	Remarks
a	72.2	*a'*	120.7	Max. *a*: not of Hg-vapor, but radiation of the hot quartz tube mercury in quartz lamp.
b	149.9	*b'*	174.5	Max. *b*: origin doubtful. Min. *a'* consists of two minima 105 and 132 μ.
c	209.9	*c'*	267.1	Water vapor absorption region in the continuous spectrum of the hot quartz tube.
d	324.8			Min. *b'*: evidently also water vapor. Max. *c* and *d* are radiation of the Hg-vapor. Min. *c*: either absorption or intermediate between selective maxima *c* and *d*.

A few more words regarding the nature of the long wave emission of mercury vapor. Since the atom [7] is not involved in the emission of a band radiation, this must be attributed to the molecule. Franck and Franck and Grotrian [8] have undertaken the study of its nature since the visible and ultra-violet spectra of mercury likewise exhibit bands; and furthermore, the phosphorescence of mercury vapor after excitation by electricity or by radiation indicates the existence of mercury molecules. Naturally, the number of such molecules present in the normal monatomic mercury vapor will be very small. We consider, therefore, that these long wave emissions are the vibration frequencies of mercury atoms combined to form a molecule, in a quasi-heteropolar union whose constituents need not necessarily be Hg-ions, but which may be merely excited (highly energized) mercury atoms. Experiments undertaken by the author on the line and band spectrum in the visible region, which are not yet concluded, point to the correctness of this explanation.

A very exhaustive investigation of the long wave radiation of mercury vapor was undertaken by G. Laski.[9] By a combination of the quartz-lens method and the filter method she succeeded in separating the radiation of the mercury vapor from that of the hot walls of the quartz tube. These experiments seem to indicate that the intensity of radiation is definitely related to the excited potentials of the mercury atom which means that excited mercury atoms, combined completely or loosely with normal atoms to form molecules, are the actual sources of the observed long wave emission.

The long wave absorption spectrum of water vapor is characterized, according to the most reliable measurements of Rubens, by the absorption bands recorded in the following table. Explanation of these long wave selective absorptions is based upon a theory of N. Bjerrum. The rotation frequencies of the molecules find expression in these absorptions;

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[7] F. A. Lindemann had already made calculations, in this connection, on the vibration frequencies of Hg-molecules which consist of Hg^+ and Hg^- ions.

[8] Zeitschr. f. Physik 4, 89 (1921).

[9] Zeitschr. f. Physik 10, 353 (1922).

the fact that these absorption ranges are limited and separated from one another by transparent regions is explainable by the quantum theory which postulates (admits) only definite rotation frequencies which an atom within a molecule may acquire upon the assumption of energy. These rotation frequencies are also in evidence in the absorption spectra of shorter wave-lengths. Here they are attributed to the mutual vibrations of the atoms in the molecule with respect to one another. Its fine structure is due to the fact that the rotational energy varies simultaneously with the vibrational energy. Thus, we may calculate, from the fine structure of the strongest absorption bands of 6.26 μ, the rotation frequencies listed in the table; similar calculations were made by E. von Bahr and W. W. Sleator, likewise based upon the fine structure of the 6.26 μ band. Rubens' measurements in the range of 22 μ–75 μ are complete, since they were measured as absorptions in a continuous spectrum of this range.

It is interesting to compare these values with those calculated on the quantum theory: the last column gives the absorption wave-lengths as calculated by Bjerrum for the quantum numbers $n = 1, 2, \cdots$ to $n = 9$. There is fair agreement only for the higher quantum numbers. We will not enter into deep discussion since this would be very indefinite at this time.

Rotation frequencies are of especial significance to the problem of the structure of the H_2O molecule—i.e., the spatial configuration of the three constituents O H H (perhaps O^{--} H^+ H^+)—since the moment of inertia of the molecule may be determined from them. Analysis of the bands obtained by means of grating dispersion for 3 μ and 6 μ seems to yield more definite information than the direct measurement of absorption (see below). For more information regarding these problems the reader is referred to the works of A. Eucken.[10]

[10] See also F. Hund, Zeitschr. f. Physik 31 (1925).

TABLE

Measured by Rubens	Calculated from the Fine Structure of the 6.26 μ Band		Calculated according to the Quantum Theory by N. Bjerrum	
	E. v. Bahr	Sleator		
19.2	19.3	—	$n = 9$	19.3
19.6	19.9	—		
20.5	20.6	—		
21.6	31.8	—	8	21.6
22.9	23.3	—		
23.8	24.3	—		
25.0	25.2	25.3	7	24.7
26.6	26.9	26.9		
28.9	28.3	28.9	6	28.9
30.6	30.6	30.6		
32.9	32.9	34.2		
35.7	35.7	36.7	5	34.7
40.9	38.8	40.3		
—	42	43.0	4	43.3
44.1	45			
—	47.5			
49.0	49.5	51.0		
57.7	55	56.8	3	57.8
65.8	62.5	65.3		
72.2	69.5	72.5		
78.0	80	81.6		
(83)				
(92)	91	92.5	2	86.6
105.8	109	101		
132.2	126	113		
175	171	135	1	173.2
256(?)	250			

Short Electric Waves

Frequent attempts have been made in recent years to penetrate and explore the long wave infra-red region adjacent to the electric waves, i.e., to produce, by means of electric resonators, waves of such wave-length as are emitted by Welsbach burners or mercury vapor lamps. The investigations along this line by Nichols and Tear and by Glagolewa-Arkadiewa seem successful; the latter particularly maintains the possibility of producing, in sufficient intensity and constancy, spectra in the range of 1 mm. to 1/10 mm. These experiments are all based upon the production of Hertz' oscillators of as small dimensions as possible. Whereas Nichols and Tear prepare these by hand, Glagolewa-Arkadiewa utilizes a suspension of finely divided metallic particles in oil which is thoroughly stirred; electrodes connected to an induction coil are immersed in the suspension; the spark discharge will thus spread over a very large number of small resonators. In this manner intensive, small electric waves are obtained.

Nichols and Tear measure their wave-lengths (1.8 mm.) by the interferometric method while Glagolewa-Arkadiewa accomplishes the same result by the heat effects on selective thermo-elements, i.e., thermo-elements active only within certain definite wave-lengths. Electric waves of 100 μ seem to have been obtained by her. An improvement of this method would in all probability lead to the solution of many molecular theoretic problems.

Long Wave Roentgen Rays

The qualitative knowledge that Roentgen rays of short wave-lengths (that is, of high frequency) are excited (produced) by electrons in rapid motion (by means of a large electronic energy) while Roentgen rays of longer wave-length are due to slow electrons and light rays to still slower moving electrons, stimulated investigation whereby it could be determined whether there was a continuous transition between the ultra-violet end of the so-called optical spectrum and the Roentgen spectrum. The quantitative relationship between wave-length and excitation according to Einstein's law made it possible to characterize (group) an observed Roentgen radiation according to its wave-length even though a direct measurement of wave-length was not possible, provided only the excitation energy was known. The quantum law applicable here is the same as we have already learned to be applicable in the excitation of optical spectra: the excitation energy of an electron of charge ϵ (elementary quantum), which has fallen through a potential difference of V volts, is ϵV. This energy is transformed into a radiation of such wave-length λ, or frequency ν, that the quantum of radiation

$$h\nu\left(=h\frac{c}{\lambda}\right)$$

is equal to the excitation energy ϵV. Numerically these energies are calculable in ergs from the relation that V volts are $1.59 \times 10^{-12}\ V$ ergs.

Proof of the existence of Roentgen rays of long wave-lengths may best be established by their activity[11] in releasing electrons (photo-electric effect of Roentgen rays). Metals exposed to Roentgen radiation give off electrons which can be measured, the metal itself assuming a positive charge which likewise is measurable. Figure 69 depicts an experimental arrangement for the investigation of such long wave Roentgen rays. Electrons from any available source proceed in the direction ϵ. They are accelerated by a field interposed between their source and the anticathode A. If Roentgen rays R are emitted by A, a photo-electric effect will be produced at M, the positive charge assumed by M being measured by means of the electrometer E.

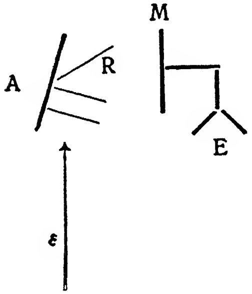

Fig. 69.

Dember[12] seems to have been the first to observe Roentgen rays of very long wave-lengths. He observed a sudden production of a photo-electric effect for a velocity of 17 volts for the primary rays, whereas electrons of slower speed excited no measurable amounts of radiation. Dadaurian[13] observed this sudden photo-electric effect for a velocity of 20 volts. E. Laird[14] and Barton, on the other hand, found

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[11] We may mention here that this method is closely analogous to Franck's method for the detection of the quantum excitation of spectral lines; see also below, Mohler and Foote.

[12] Verh. d. Deutsch. phys. Ges. 15, 560 (1913).

[13] Phys. Rev. 14, 234 (1919).

[14] Phys. Rev. 15, 293 (1920).
Phys. Rev. 15, 297 (1920).

a radiation only for velocities above 190 volts and they attribute the results mentioned above to ionization of residual gas. Laird and Barton propose likewise to investigate the nature of this Roentgen radiation: is it a continuous spectrum or a characteristic (line) spectrum? Since they obtained essentially the same radiation for brass, platinum, graphite, aluminum, and lithium anticathodes, they assume the radiation to be a continuous spectrum, whose wave-length range depends only upon the electronic energy and not upon the emitting substance. They eliminate the source of error mentioned above—measurement of ionization of residual gas instead of the number of electrons emitted—by interposing between the anticathode and the measuring chamber a very thin celluloid window (screen). It is indeed beyond doubt that the absorption in this window (screen) has prevented the detection of still longer Roentgen rays: the Roentgen rays arising from *A* are of such long wave-length that they cannot penetrate the screen and arrive at the measuring chamber. We must mention, here, that Dadaurian as well as Kurth (see below) have very carefully avoided these sources of error.

Richardson and Bazzoni[15] made slow moving electrons impinge upon anticathodes of carbon, molybdenum, copper, and tungsten, and found for critical velocities of the former a strong emission of Roentgen rays. The quantitative data are as follows: for carbon, a sharp radiation sets in at 286 volts; for molybdenum, between 354 and 358 volts.

Dadaurian[16] also obtained indications of a line emission in addition to the photo-electric (or, as he called it, radio-electric) current of the continuous Roentgen spectrum. Thus, it was found that maxima of the photo-electric current arose for critical electronic velocities; for a platinum anticathode this was 400 and 580 volts, and for copper, 800 volts.

E. H. Kurth[17] continued these investigations and he obtained a large number of sharp breaks in the photo-electric

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[15] Phil. Mag. 42, 1015 (1921).

[16] Phys. Rev. 14, 234 (1919).

[17] Phys. Rev. 17, 528 (1921); 18, 99 (1921).

curves for reproducible critical electron velocities. From these he calculates, with the aid of Einstein's formula, the wave-lengths of the rays which he recognizes as a characteristic series.

Wave-lengths computed from these excitation potentials according to Einstein's equation lie in the region of approximately 50 to 500 Å. On the basis of Moseley's law, which expresses the linear relationship between the atomic number of the elements and the square root of the frequency of the characteristic Roentgen radiation of the same series, the wave-lengths so computed may be grouped in appropriate series. If the K-radiation of a higher element of atomic number Z be equal to ν_k, the frequency ν_k' of a lower element of atomic number Z' is calculable from the relation $\frac{\sqrt{\nu_k}}{Z} = \frac{\sqrt{\nu_k'}}{Z'} = \text{constant}$, or $\lambda Z^2 = \text{constant}$. We will refrain from a restatement of these computed wave-lengths since further mathematical and theoretical evaluation of these still too indefinite data has not been forthcoming.

The parallelism [18] between the measurement of optical and Roentgen ray excitation energies is more marked in the experiments of Foote and Mohler, in which electrons of increasing velocities entered into a metallic vapor (sodium, potassium, magnesium), the photo-electric charge being measured, as in the method of Franck, by means of the radiation of the excited vapor atoms. However, their results offer only qualitative evidences of a higher frequency than that of the optical series inasmuch as sudden emission of radiation as well as ionization phenomena were obtained with a higher critical potential. The results will be utilizable quantitatively only when the "Roentgen ionization" has been separated from the "optical ionization."

Worthy of mention also are the experiments of Holweck [19] which were carried out with apparatus similar to that of Laird, i.e., apparatus in which the measuring chamber was

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[18] See note, p. 294.

[19] Holweck, Compt. rend. 171, 849 (1920); 172, 439 (1921).

screened off from the electron source by means of a celluloid sheet. The latter was only about 2.5×10^{-5} cm. thick. Radiation was measured down to 25 volts excitation energy ($\lambda \sim 493$ Å.). Strong absorption maxima in the celluloid foil are measured between 40 and 10 Å. (K-absorption) and for 320 Å. (L-absorption), both in agreement with the emission wave-lengths of carbon. It is noteworthy, also, that the celluloid foil, which practically consists of carbon only, was much more transparent to the relatively long waves of about 1,000 Å. (Lyman series of hydrogen) than to the shorter wave-lengths of 320 Å., a proof that a characteristic absorption, viz.: that of carbon, actually is taking place in the latter case.

If we review these investigations as a whole, we shall perceive the experimental evidence of the existence of very long range characteristic Roentgen ray spectra. The transition into the optical region is fully accomplished: the shortest optical waves emitted by gases and vapors and measured with gratings lie at 150 Å., while the longest Roentgen rays emitted by solid bodies lie between 300 and 400 Å., wave-lengths successfully detected by means of optical gratings by R. A. Millikan.

We will omit discussion of the region of normal Roentgen emission, the regularities of the K-, L-, M-, etc., series, and turn our attention to the short wave end of the spectrum. According to our usual conception of the emission phenomenon, the K-series of an element should be its shortest characteristic radiation or specific radiation, i.e., it should be the high frequency end of all possible monochromatic or line or series emissions. Only the continuous Roentgen spectrum, whose high frequency boundary is influenced in no way by the structure of the atom and depends only upon the energy of the exciting electrons of the cathode rays, can have still shorter wave-lengths. A characteristic radiation of smaller wave-length than the K-radiation must be one which arises because of some direct action by the atomic nucleus, somewhat in the manner that γ-radiation arises during radioactive nuclear disintegration.

J-Radiation[20]

Much uncertainty prevails regarding the existence of characteristic atomic frequencies greater than those of the K-series. Barkla and White[21] concluded, on the basis of absorption measurements, that aluminum possesses a very "hard" specific radiation. Numerous subsequent investigations[22] by other experimenters yield contradictory results which may be summarized somewhat as follows: J-emissions have not yet been observed spectrometrically; the absorption coefficients of light elements give no evidences of an anomaly, or only an extremely small anomaly, in the region of shorter wave-lengths than the K-radiation of the absorbing substance. In such instances where an anomaly was found, there is a possibility that the absorption substance (lighter elements) was contaminated by the presence of heavier elements. The secondary radiation of light atoms seems to contain a portion of "harder" radiation than the K-radiation, although the dispersed radiation has not been investigated spectrometrically, but only by absorption analysis, i.e., the wave-lengths are determined from the absorption coefficients of the radiation concerned in aluminum by substitution in an empirical formula. The wave-lengths cited below for the radiation have been obtained in this way.

We will discuss these results briefly in the light of the investigations in question. Duane and Shimizu[23] examined spectrometrically (with ionization chamber) the radiation of a Coolidge tube with 71,000 volts and having an aluminum anticathode in the region of 0.182 to 1.259 Å. The characteristic radiations (spectral lines) present in their curves are derived from secondary influences: from molybdenum (present

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[20] Although it is assumed frequently that the discovery of the Compton Effect (Chap. XVII) has solved the problem of J-radiation, we nevertheless will repeat here the statements made about J-radiation in the first edition of this book. Complete clarity is still wanting.

[21] Phil. Mag. 34, 270 (1917).

[22] Williams, Proc. Roy. Soc. 94, 567 (1919); Owen, Proc. Roy. Soc. 94, 339 (1919); Houston, Proc. Roy. Soc. Edinburgh 40, 34 (1919).

[23] Phys. Rev. 13, 289 (1919); 14, 389 (1919).

in metallic form in the tube) whose K_α- and K_β-lines appeared and from the L_α- and L_β-lines of lead (screen radiations). No trace was found of a line radiation of aluminum in this short wave region (K-radiation of aluminum is 8 Å.). Dauvillier[24] and Ledoux-Lebard and Dauvillier[25] found a similar result with a boron anticathode, i.e., no characteristic radiation was emitted between 0.2 and 1.0 Å.

With aluminum as the absorbing substance Dauvillier[26] observed a recognizable variation of the absorption process at 0.358 Å., whereas Richtmeyer was unable to detect such a phenomenon. Richtmeyer[27] likewise was unable to confirm the following absorption regions determined indirectly by other observers (spectrometric measurements): water 0.39 Å. (Barkla and White), bromine 0.227 Å. (Dauvillier), silver 0.178 Å. (de Broglie). Indicative of the uncertainty of these results is the fact that Barkla and White and Dauvillier find J-absorption in aluminum at 0.37 Å. and 0.358 Å. respectively, while Williams observes absorption both in aluminum and in copper at 0.49 Å. Finally, Hewlett reports no J-absorption between 0.2 and 1.5 Å. for water, lithium, carbon, nitrogen, oxygen, aluminum and copper.

Crowther[28] investigated the dispersed radiation of paraffin, aluminum and copper. The dispersing substance Z in the form of thin lamina is inclined 45° to the primary radiation. The radiation *a* (in the direction of the primary ray) and radiation *b* (perpendicular to the primary ray) are measured by means of two ionization chambers. Aluminum leaflets are interposed in front of the chambers, whose thicknesses are varied for the determination of the absorption coefficients of radiations *a* and *b* (Fig. 70).

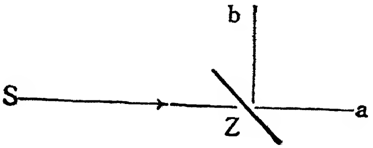

Fig. 70.

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[24] Annales de Physique 13, 49 (1920).

[25] Compt. rend. 168, 608 (1919).

[26] Annales de Physique 13, 49 (1920).

[27] Phys. Rev. 15, 287 (1920); 17, 433 (1921); 18, 13 (1921).

[28] Phil. Mag. 42, 719 (1921).

The radiation in the direction *b* was found to be "softer" than that of direction *a*; for it was absorbed more strongly. The wave-lengths are determined from the measured absorption coefficients in both directions; a direct measurement of wave-length does not occur. The results are listed in the following table.

	Primary Wave-lengths Calculated from Absorption in Direction *a*	Dispersed Wave-lengths, Direction *b*
Paraffin	0.38 Å.	0.43
Aluminum—1st expt.	0.41 Å.	0.51
2d expt.	0.36	
Copper	0.36	0.46

The wave-lengths given in the last column are considered to be those of J-radiation. It is very difficult to state whether the existence of J-radiation is hereby established. If we reflect that there is still so much uncertainty regarding the dispersion of Roentgen rays, we cannot rely too confidently upon the evidences of Crowther's experiments. Thus, we do not even know the various ways in which a monochromatic radiation may change its wave-length during dispersion; nor do we know just how much long wave characteristic radiation of the dispersing substance is contained in the dispersed radiation. Barkla and Sale also, as the result of new experiments, are not quite sure of the existence of J-rays, although they do not definitely commit themselves. However, the entire problem—at least as far it deals with wave-length measurements of the dispersed radiation—must be considered from an entirely different viewpoint since A. H. Compton has demonstrated a real change in wave-length during dispersion. This was discussed in Chapter XVII. Barkla vigorously and vehemently opposes Compton's explanation: by maintaining J-discontinuity, he explains Compton's variations in wave-lengths as a consequence of the absorption of the radiation in the dispersing substance. However, the definiteness of Compton's results no longer admits of such an interpretation.

It was shown in Chapter XVII that precisely the results of the Barkla-dispersion are explainable by means of Compton's dispersion. Naturally, it cannot be claimed that Compton's dispersion comprises all dispersion anomalies.

Obviously, the method employed is, in the first place, a determining factor as to whether or not J-radiation will be obtained—and this is not always decisive and conclusive for the reality of an "effect." Furthermore, the authors who have decided in favor of the existence of J-radiation have never carried out a direct measurement of its wave-lengths, but have computed the wave-lengths of this supposedly characteristic radiation only indirectly from anomalous absorption coefficients according to an empirical relationship between absorption and wave-length which is not valid especially in the neighborhood of a characteristic absorption (average values of wave-lengths). Siegbahn and Wingarth [29] likewise conclude that an anomalous absorption in this disputed region of J-radiation in no way is definitely established.

An eventual successful demonstration of the existence of J-radiation does not, of necessity, mean the abandonment of Bohr's atom theory or of Kossel's [30] explanation of Roentgen spectra. An eventual J-emission does not even appertain to Kossel's scheme. Nevertheless, it seems that an explanation of J-discontinuity in the absorption as a relative monochromatic absorption is not altogether excluded if an electronic sphere, e.g., the K-ring, were doubly ionized. Furthermore, to associate this radiation with a nuclear radiation is likewise not impossible, i.e., we may regard this radiation as a type of "enforced radioactivity." In this connection the recent researches of Crowther [31] are especially interesting; they are based upon Rutherford's investigations on the relationship of β-rays and γ-rays in radium C, which were recently continued by Lise Meitner and Ellis.

The frequencies of γ-rays are, in part, much higher than

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[29] Physik. Zeitschr. 21, 83 (1920).

[30] See Kossel's "Valence Forces and Roentgen Spectra" (pub. by Springer, 1921).

[31] Phil. Mag. 42, 719 (1921).

the characteristic K- and L-radiations of radium C whose similarity to the soft rays has been demonstrated. It is indeed possible, therefore, that a J-radiation corresponding to the hard γ-rays can be excited in the lower elements. It may be, also, that not all the lighter elements can emit this radiation, and—assuming J-radiation as a nuclear radiation—that it is associated with a peculiar grouping of the elemental constituents of the nucleus. If we assume that the J-radiation frequencies are related to the atomic numbers of the elements in somewhat the same manner as the K-, L-, and M-series, that is, proportional to the square of the atomic number (Moseley's law), the wave-lengths calculated for aluminum ($Z = 13$) from the atomic number of radium C would be 27×10^{-8} to $.24 \times 10^{-8}$ (frequencies $\nu = c/\lambda = 1.09 \times 10^{18} - 12.6 \times 10^{18}$ sec.$^{-1}$). In other words, this means, contrary to the K-, L-, and M-series, an expanded series of very wide frequency range. Excitation of this J-radiation would take place according to Stokes' fluorescence or according to Einstein's quantum law but without the limitations which experience has shown to apply in the K-, L-, ···, emissions, viz.: that a series can be excited only in its entirety and by an energy ($h\nu$) which is greater than that of the characteristic lines and which coincides exactly with the boundary of the series. Only in this way could the dependence of the emission frequencies of the so-called J-radiation upon the exciting radiation energy at best be intelligible.

It would be most significant conclusively to establish the existence of J-radiation. For the present, we may characterize our experiments as too incomplete and imperfect to base theoretical conclusions upon them or even to abandon such well-established viewpoints as those on the localization of the emission excitation of the Roentgen series in the atom.

CHAPTER XIX

THE PHOTO-ELECTRIC EFFECT

When electromagnetic radiation of proper wave-length impinges upon a metal, a part of the absorbed radiation is consumed by the metal to disengage electrons from it. By "proper" radiations is meant here all short wave-lengths (optical radiation, X-radiation, γ-radiation) below a certain limiting long wave which is characteristic for each metal. All these "proper" radiations possess this capability. If the metal is insulated, it will become positively charged under the influence of the radiation as a consequence of the loss of a negative charge. That the negative discharge proceeds in the form of electrons is established by determining the specific charge of these electricity carriers and also by the direct measurement of the charge assumed by ultra-microscopic particles. The electrons leave the metal with a definite velocity. They likewise receive this kinetic energy from the radiation according to Einstein's quantum law. If ν designates the frequency of the exciting radiation and h the universal constant, the energy of a radiation element (unit) $h\nu$ is equal to the kinetic energy of the electron $\frac{1}{2}\mu v^2$. But since all the radiation energy cannot be transformed into kinetic energy of the electron, since the latter consumes a fixed amount of it during its disengagement from the metal, $\frac{1}{2}\mu v^2 = h\nu - A$, wherein A designates the liberation energy. It is the minimal radiation energy capable of bringing about a photo-electric electron emission; and this minimum energy quantum $h\nu_0$ may be observed in the long wave limit of the photo-electric excitability. The complete law is therefore:

$$\tfrac{1}{2}\mu v^2 = h(\nu - \nu_0); \qquad \text{or} \qquad v = \sqrt{\frac{2h(\nu - \nu_0)}{\mu}};$$

i.e., v is the velocity of an electron liberated by frequency ν.

The principles of the quantum theory have been confirmed, as is known, by many extensive experimental investigations. We shall here discuss another problem, the problem of the source (origin) of the electrons. Completely to treat this—we may add, still unsolved—problem, a preliminary remark is necessary. In the previous paragraph we had outlined the general photo-electric phenomenon. There are, however, two distinct types designated usually as the "normal" and "selective" photo-electric effects, respectively. The latter is distinguished from the normal by having a definite frequency, characteristic for each metal, with which a copious disengagement of electrons may be obtained. This is related not only to the critical frequency but also to a definite polarization state of the exciting radiation, i.e., the electric vector of the exciting radiation must be polarized in the plane of incidence.

In the following we will discuss primarily the normal photo-electric effect. The quantum theoretical formulation of the photo-effect, due largely to A. Einstein, makes the velocity of the liberated electrons proportional to the frequency of the exciting radiation. Another relationship, however, will be apparent if the number of liberated electrons are referred to equal amounts of absorbed radiation. Let the radiation consumed in the liberation of electrons (we assume it proportional to the absorbed radiation) expressed as energy be S; if its frequency is ν, the energy causing the release of electrons will be $h\nu$ and the total energy S will contain n such energy units, or $n = S/h\nu$. In other words n electrons should be liberated. If a higher frequency ν' be used (shorter wave-lengths) in place of the frequency ν, the radiation S will be comprised of $n' = S/h\nu'$ quanta, where $\nu' > \nu$, and $n' < n$. The number of liberated electrons should decrease, therefore, with increasing frequency of the exciting radiation, an expectation which is not borne out by experiment; on the contrary, an opposite effect is always observed, viz.: increase in the magnitude of the "photo-stream" (liberated electrons) with decreasing excitation wave-length (increasing frequency).

The existence of a long wave excitation limit in conjunction with the velocity-frequency proportionality offers a solution for this contradiction. This long wave boundary is related to a definite "austrittsarbeit"—work of emergence—of the electron from the illumined surface. This may be divided into work done during the release of the electron from a metal atom and work done in the emergence of the electron from the metal surface. The latter will depend entirely upon the surface conditions—but it is not yet possible physically to describe a "surface," i.e., to specify the conditions influencing the emergence of the electron from the surface. No matter what these may be—there can be no doubt that an electron released from a metal atom can overcome this opposing force so much the easier the greater its primary velocity, that is, the velocity imparted to it upon disengagement from the atom. In other words, it will be the greater the greater the frequency of the exciting radiations. Thus the number of electrons actually ejected—and these only can we observe—becomes the greater the greater the frequency of the exciting radiation, owing therefore to this subsidiary circumstance, which is not necessarily related with the effect as such. The quantum prerequisite is always expressed only in the energy balance of the individual elementary process, but not in its useful effect. In other words, the performance of the process is indeed in accordance with the quantum law, but whether it will ensue or not, depends upon other conditions, for the most part not yet known.

This gives rise simultaneously to the problem of the influence of surface on the photo-electric effect. The significance of gaseous films and films of moisture adsorbed on the surfaces of metals (the so-called "gas films" and "water films") is known to us from many other physical phenomena. It seemed reasonable, therefore, to probe into the influences of high vacua and thorough drying upon the photo-electric effect. Discussion of a controversial nature has centered on this problem during the last decade which does not appear to have been clarified in spite of extensive investigations.

W. Hallwachs and his coworkers, especially, are of opinion, as the result of many experiments, that gas and water films adsorbed on a metal lower the intensity of the photo-electric electron stream, but that the "photo current" not only does not increase with increased extraction of gas from the metal but is diminished, on the contrary, to small fractions of its initial value. We understand this result as signifying that the normal photo-effect is connected with a combination of gas and metal, and that therefore—after its destruction by a continued incandescence of the metal—the release of electrons ceases to a great extent, if not entirely.

The influence of superficially adsorbed films is intelligible; they intercept the electrons as soon as they emerge from within the metals; whether this effect is "mechanical" or "electrical" is not quite definite. The influence of such surface layers is plainly in evidence in the experiments of Millikan and Souder in which it was shown that progressive oxidation of magnesium (although this oxidation was not noticeable exteriorly) brings about a displacement of the long wave boundary of the photo-electric effect to shorter waves; in other words, progressively larger energies are necessary to get the electron through the surface. Krüger as well as Pohl and Pringsheim have indicated emphatically a connection of these phenomena with the contact potential. S. Taubes has investigated the long wave boundary of the photo-electric excitability of mercury particles of ultramicroscopical subdivision. However, these possess "pure" surfaces, according to more recent research, only as long as they vaporize.

The nature of the photo-electrically sensitive gas-metal compound, as proposed by Hallwachs, is wholly unexplained. It is quite natural to call to mind many well-established metallographic relations that deal with the variations in the intrinsic characteristics of a metal induced by the presence of gas in them. For example, iron containing hydrogen is very "hard" magnetically, whereas hydrogen-free iron is very soft. Furthermore, electrical conductivity depends on the gas content, a fact which obviously points to an appreciable influence upon the manner in which electrons are "bound" in a "gas-metal" union. We believe, furthermore, in recognizing in this connection another phenomenon investigated in recent times in relation to other physical reactions. A. Janitzki[1] has demonstrated that when metals exhaustively purified from gas are utilized as cathodes in X-ray tubes, an independent discharge will take place only at the application of abnormally high discharge potentials. H. Stücklen[2] observed that the minimum spark potential at first becomes smaller as metals are progressively dried and freed from moisture films, but with prolonged drying an increase in the spark potential again sets in. This is evident from Figure 71 in which the "release" potentials (minimum potential) are represented as functions of time of drying.

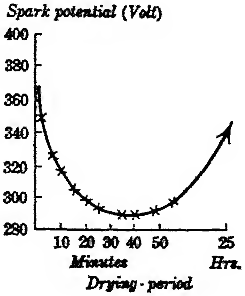

FIG. 71.

It is evident that in these phenomena we likewise find it increasingly more difficult for the electron to free itself from the metal as the gas and moisture content of the metal is progressively diminished. Nothing can be said at present regarding the nature of these influences. It may be feasible to consider another phenomenon in this connection. K. Fajans and W. Frankenberger have demonstrated recently in a rather significant experiment that adsorbed ions enhance the photo-chemical sensitivity of silver bromide to so considerable an extent that it can be decomposed by radiations of longer wave-lengths. This decomposition doubtlessly results from a photo-electric effect; and, indeed, under the influence of the illumination, a negative bromide ion of the silver bromide molecule seems to give up an electron with the formation of elementary bromine. To accomplish this a fixed amount of light energy, i.e., a definite quantum $h\nu$, is necessary. Due

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[1] A. Janitzki, Zeitschr. f. Phys. 11, 22 (1922).

[2] H. Stücklen, Ann. d. Phys. 69, 625 (1922).

to the adsorbed ions the work required to liberate an electron from the negative bromide ion is diminished, as a consequence of which a smaller light quantum $h\nu$, that is, a longer wavelength, will suffice. We recognize in this (along with Fajans) an electrostatic disturbance of the surface structure. By analogy, a similar procedure should bring about the variations in the work of detachment ("Ablosearbeit") and the work of emergence ("Austrittsarbeit") noted in photo-electric phenomena.

That a characteristic "form" of the metal, at least of the surface, is due to its gas content, may be evident from the following experiments[3] which however have not yet been corroborated. The selective effect—the previously mentioned maximum electronic yield obtained for a definite frequency which hitherto had been considered characteristic of the metal—is not characteristic of the metal but rather of the gas-metal combination. A displacement of the maximum by gases had already been observed by Pohl and Pringsheim. Wiedmann finds that potassium when sufficiently purified from gas no longer shows a selective effect which it exhibited previous to purification at $\lambda = 436\ \mu\mu$. Addition of oxygen brought about a new selective effect at $\lambda = 313\ \mu\mu$ which receded extensively at subsequent heating in high vacuum. The maximum at $436\ \mu\mu$ is ascribed to the influence of hydrogen. Since the data of various observers on the position of the maximum of the selective effect for the other alkali metals do not agree, Wiedmann infers the influence due to the presence of gas, the position of the maximum in any case being conditioned upon the nature of the gas accidentally contained in the metals of the respective investigators.

Fr. Groos[4] examined metallic films produced in vacuum by cathodic comminution and found positive indications of selective effects for copper and gold. Upon the introduction

[3] G. Wiedmann, Jahrb. d. Rad. u. Elektr. 1922. A rather comprehensive exposition, from the viewpoint of Hallwachs' theory of the variation of the photo-electric behavior of the metal with varying amounts of gas.

[4] Fr. Groos, Zeitschr. f. Phys. 6, 376 (1922); 31, 637 (1925).

of air, the selective effect for copper disappeared completely (the excitation produced by light vibrating parallel to the plane of incidence became equal to the excitation produced with light vibrating perpendicular to the plane) and for gold it became less pronounced. In more recent experiments he showed that copper films prepared by volatilization have a very weak selective effect, or none at all, merely because they are not precipitated "gas-free" by these methods.

Sodium films obtained by the condensation of atomic rays show marked selective effect, which disappears, however, with the absorption of gas by the sodium layer. Films, whose thickness is far below the range of visibility, give evidences of the photo-electric effect (unpublished experiments of the author and E. Zimmer).

In passing we make reference to the theoretical calculation of the position of these maxima by Fr. Groos.[5]

The Independence of the Photo-electric Effect of Temperature.

This may be considered as definitely established. Naturally, secondary effects can readily simulate and be mistaken for temperature effects. Thus, A. G. Shenstone[6] found a remarkable increase of the photo-electric effect for bismuth when this is heated by means of an electric current. Shenstone assumes this to be due to temperature influences. The experiments are, however, in no way conclusive. We may mention that even errors of large proportions are possible; for example, the warming of adjacent parts of the vessel by heating of the metal. These heated portions thus evolve gas which is ionized by the accelerated photo-electric electrons; in this wise, the current is intensified due to this impact-ionization. Control experiments to cover such secondary phenomena or other eventualities are entirely wanting in Shenstone's experiments.

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[5] Fr. Groos, Zeitschr. f. Phys. 7, 316 (1922).

[6] Shenstone, Phil. Mag. 41, 916 (1921).

The Dependence of the Photo-electric Effect on the Magnet Field.

Such a dependence was found by Dember[7] in bismuth when illuminated with ultra-violet radiation. Here, also, secondary influences may be operative, for it is indeed possible that the paths of the liberated electrons, and not the photo-electric emission process, are modified by the magnetic field (as is well known), which is easily noticeable in the variations of the measured current.

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[7] H. Dember, Physik. Zeitschr. 21, 568 (1920).

CHAPTER XX

PRACTICAL APPLICATIONS OF THE PHOTO-ELECTRIC EFFECT

The work of H. Rosenberg[1] on the properties of photo-electric cells and the combining of photo-cells with amplifying tubes represents a very important and marked progress in the photo-electric photometry. Photo-electric photometry is based upon the proportionality of electronic stream to absorbed light quanta. In the first place, therefore, attention must be centered upon the constancy of absorption. This is particularly true if light sources are to be measured with different colors. Objections have been raised repeatedly against the photo-electric proportionality law although numerous investigators have endeavored to offset these opinions. In this connection particular mention may be made of the comprehensive work of Elster and Geitel. These observers showed the validity of the proportionality law for a large range of light quantities although the comparison did not extend over large intervals. Expressed more carefully, their result would be somewhat as follows: for not too great fluctuations of light energy a proportionality exists between the photo-stream and the quantity of light, independent of the absolute amount of the light energy. But even under these conditions there are departures from the proportionality which, in Elster and Geitel's experiments for an intensity relationship of 1 : 2, amounted to about 0.5–1 per cent. Such limits of error are too large for many cases, especially since this error is not constant, its magnitude depending entirely upon the various external and internal conditions of the cell arrangement.

H. Rosenberg, accordingly, has undertaken recently the tedious problem of examining very minutely the "mechanism" of Elster-Geitel's supersensitive alkali photometer cell and

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[1] H. Rosenberg, Zeitschr. f. Physik 7, 18–64 (1921).

has obtained data which is of great significance for the correct utilization of cells in exact photo-electric photometry. Steinke[2] recently has confirmed the essentials of Rosenberg's findings and in part has extended them.

We shall consider first that result of Rosenberg's investigations that is of greatest importance theoretically. High vacuum cells, as well as gas-filled (inert gas) cells, with sensitive alkali metal cathodes, show a strict proportionality with an accuracy 1/10 per thousand between the quantity of light and the pure photo-effect for all applied potentials, even in the neighborhood of the discharge potential. This proportionality is vitiated, however, by the introduction of secondary influences, as the so-called fatigue and recovery phenomena, the vitiation being the greater the closer the cell potential lies to the discharge potential, i.e., the more sensitive the means of measurement. In practice, therefore, deviations from this proportionality must be considered under all circumstances. In addition to these deviations there are variations in the sensitivity of the photo-cell. However, these may be sufficiently restricted if provision be made that the accelerating potential be applied to the cell for a sufficient interval before the beginning of the measurements, and that an equilibrium—with respect to exchange of gas between the metal and the surrounding atmosphere—has been established in the cell by sufficient preliminary illumination. Steinke found that a relation existed between the photo-stream J and the intensity of light L in the case of his Elster-Geitel "mirrored" potassium cell (prepared by Gunther and Tegetmayer in Braunschweig from whom it may be obtained) after a sufficient preliminary fatigue (that is, after the establishment of Rosenberg's equilibrium). This may be expressed as $J^z = \mathrm{C.\,L.}$ Z is the cell constant, which is always greater than 1, and greater, the nearer the cell potential approximates the discharge potential. Since the discharge potential varies with the time even in the dark, as found by both Rosenberg and Steinke, Z likewise varies as does the

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[2] Steinke, Zeitschr. f. Physik 11, 215 (1922).

relation between J and L. The constant Z is dependent not only on the discharge potential but on the wave-length of the exciting light as well, as is evident from the values reported by Steinke (Fig. 72). It is evident from these data that the influence of the potential as well as the influence of the wave-length will be the more pronounced, the more sensitive the cell utilized. Even though these last described phenomena are not common to all cells, but peculiar only to a definite cell, it becomes the more evident how urgently we must be cautioned against a careless performance of photo-electric photometric measurements.

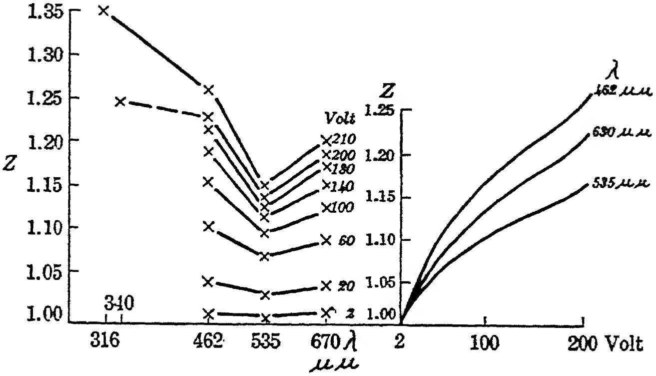

FIG. 72.

These complicated relations caused Rosenberg to develop a photometric method in which the cell is used only as a "null instrument" of high sensitivity. Instead of utilizing the scale reading of the measuring device attached to the cell as a measure of the intensity of the radiation to be measured photometrically, the action of this radiation is compared to that of a "comparison" radiation of known luminosity which can be diminished to fractions of its total value by means of two rotating Nicols. To insure the requisite preliminary fatigue, i.e., to establish the so-called equilibrium conditions, the cell is previously illuminated with a radiation of approximately the same luminosity as that to be photometrically measured until the photo-sensitivity is constant. Should a cessation of illumination set in because of variations in the source of radiation, the interruption in the cell illumination must be avoided under all circumstances, and compensated for, by the introduction of the comparison cell during the cessation interval.

The accuracy obtained by Rosenberg with this method is very great; he succeeded in measuring luminosities with an error of about ± 1 part per thousand for individual measurements. This corresponds—in ordinary astronomical units—to an uncertainty of 0.00063.

The utilization of photo-cells in conjunction with amplifying tubes[3] has been studied almost simultaneously by many investigators.[4] This method was investigated very thoroughly and in detail by Rosenberg.[5] The amplifying tube contains an incandescent filament for the production of electrons (cathode), an anode and a gauze electrode placed between the two former. A potential is applied across cathode and anode; the anodic stream passing through this circuit is dependent in intensity upon the potential of the grating electrode. This "regulates," according to its magnitude and sign of its charge, the intensity of the anode stream. The "directive potential" furnishes the negative charge of one of the electrodes of a photo-cell which is proportional to the illumination. There results the following circuit which requires no explanation. The circuit designated "Compensation" serves for making measurements. Equalization of the current by means of the variable resistance inserted in it makes it possible easily to compensate for the "tube" current flowing through the galvanometer *G*. If this varies because

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[3] Vacuum tubes used in wireless telegraphy; for details see P. Lertes, Forschungsberichte, Vol. 4.

[4] The first publication known to the author is "Microphotometer," patent 316,170 Kl. 42 h, Gr. 17–19, IX, 1918, Siemens and Halske A.-G. C. E. Pike, Phys. Revue 13, 102 (1919), whose arrangement was adopted by Rosenberg, Abraham and Bloch, Compt. rend. 168, 1321 (1919); E. Meyer, H. Rosenberg and Tank, Arch. d. Sc. Nat. 1920.

[5] H. Rosenberg, "Die Naturwissenschaften," Vol. 19–20 (pub. by Springer, Berlin, 1921). All the essential points are discussed here. A newer investigation with more suitable tubes: Du Piel, Ann. d. Physik (1922).

of the change of the grating potential connected with the photo-electric charge of the photo-cell, the compensation will be disturbed and the galvanometer will indicate a throw of the needle proportionate to the intensity of the illumination.

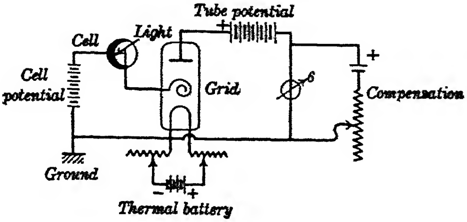

FIG. 73.

Amplifications obtained in this manner are extremely large; under favorable conditions a 600,000-fold amplification of the photo-electric current may be obtained. The method elaborated at the observatory at Oesterberg (Tübingen) is utilized for photometric measurements of stars. Extensive measurements have been carried out by Guthnick and Prager at the Neubabelsberg Observatory. We may form an approximate idea of the progress attained from the fact that it is possible to generate, from the light of the planet Jupiter, currents of 10^{-4} to 10^{-5} amperes.

It is essential for the usefulness of this method that the individual parts of the amplifying tubes be well and excellently insulated. To accomplish this effect, Siemens and Halske have devised an interesting tube-construction. The lead to the grating is conducted through the best insulator, amber; but since lutes must be avoided and amber is not fusible with glass, the lead is conveyed through an especially evacuated gas-lug carrying at its side a drying vessel; this is charged with a drying substance, e.g., calcium chloride, which removes the poorly insulating film of moisture from the glass of the apparatus. This is an interesting technical application of familiar laboratory methods.[6]

In connection with our discussion on the amplification of

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[6] Patent, Kl. 21 g, Gr. II, Nr. 391,232, 30, X, 1921.

photo-electric currents we may mention the work of K. W. Hausser, R. Jaeger and W. Vahle,[7] which likewise deals with the re-enforcing of weak ionic currents. These authors state that it is very essential to use as small anode potential as possible (above figure: tube potential), if the amplifying tubes still contain traces of gas. Otherwise, variable currents of positive ions, produced by the impact of electrons upon the residual gas atoms, will continuously arise in addition to the electron current. They do not exceed 7 volts in their "tube galvanometer."

The Photo-electric Photometry of Photographic Pictures.

This is due largely to the researches of P. P. Koch [8] extending over a period of years. Koch has succeeded in constructing, with the aid of photo-electric cells, a photometer (capable of being used also as an automatic registering device) which is useful for many purposes. The method employed rests upon the photo-electric measurement of the photographic impressions produced by the radiation of an incandescent lamp when transmitted through closely placed points. Since these ranges can be taken exceedingly small, while the registering device provides for a corresponding magnification, it becomes possible to observe the utmost nuances in the course of the darkening, e.g., of a spectral line. By making efficient use of all its possibilities, the method will develop a serrated or jagged curve when photometrically measuring a uniformly continuous "blackening" of a plate; the jags give evidence of the microscopic fluctuations in the extent of darkening as a result of the random distribution of the silver bromide granules, a proof of the sensitivity of the method. Figure 74, a photograph of such a recording of darkening (in this case, the absorption photographs of the D-lines of sodium in the continuous spectrum), is a typical example.

Since doubts arise time and again whether the alternate

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[7] Publication of Siemans Co., 1922.

[8] See, above all, P. P. Koch, Ann. d. Phys. 39, 705 (1912); F. Goos, Zeitschr. f. Instrumentenk 41, 313 (1921); Physik. Zeitschr. 22, 648 (1921).

illumination of the cell in Koch's photometer does not cause a distortion (as fatigue phenomena, variations in sensitivity and similar effects) of the true distribution of "blackening," Rosenberg recently constructed a photometer with photometric cells for photometrically measuring photographic plates ("Electrophotometer" constructed by "Askania Werken," Berlin). This device contains the photo-cell merely as a "null" instrument. The principle underlying its use is somewhat as follows: the ray of light passes successively through the plate which is to be photo-measured and an absorption instrument, i.e., a blackened wedge-shaped device,[9] then impinging upon a photo-electric cell. The deflection of the attached electrometer is compensated—by the method of P. P. Koch—by a second photo-electric cell placed in opposition to the first. We thus eliminate almost entirely fluctuations in the intensity of the source of light. If, as a result of the moving the photographic plate through

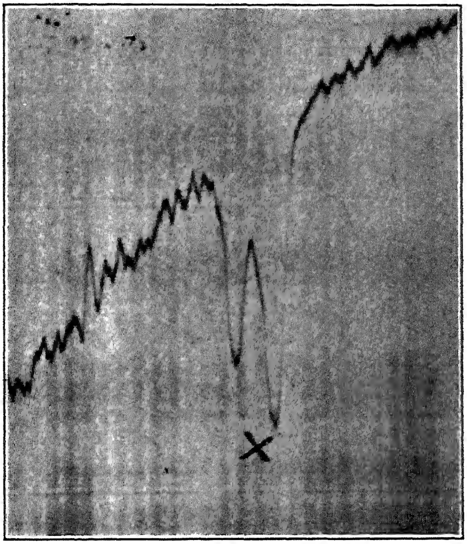

FIG. 74.

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[9] Or two rotating Nicol prisms.

the ray of light, various darkenings are introduced into the latter, the wedge is subsequently adjusted in such manner as to keep the electrometer constantly at zero. The reading of the position of the graduated wedge of darkening will indicate the darkening of the plate, point for point. It is apparent that the photo-electric cell will be constantly subjected, throughout the process of measurement, to the same intensity of radiation.

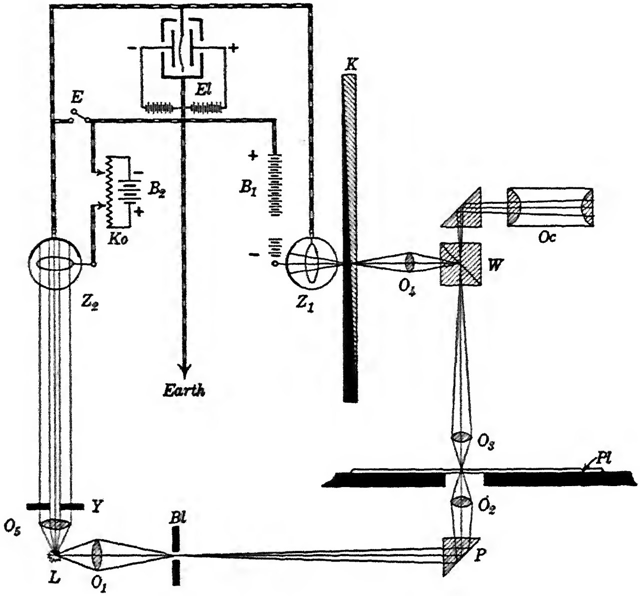

FIG. 75.

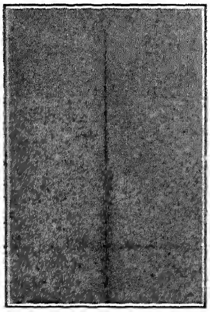

FIG. 76.

The arrangement will be understood from Figure 75. Two light rays emanate from the incandescent lamp *L*; one by way of O, PO_2O_3, through the photometric plate *Pl*, to a small silver mirror in the cube *W*, from which it falls through O_4 and the wedge *K* upon the measuring photo-electric cell *Z*; the second ray impinges on the compensation cell Z_2. By means of the eyepiece *Oc′* the object to be photo-measured, whose image lies in *W*, may be seen directly, for precise adjustment, for instance. The electric circuit requires no comment, being clear from the figure. A highly sensitive (e.g., a Wulf) single-filament instrument is used as electrometer.

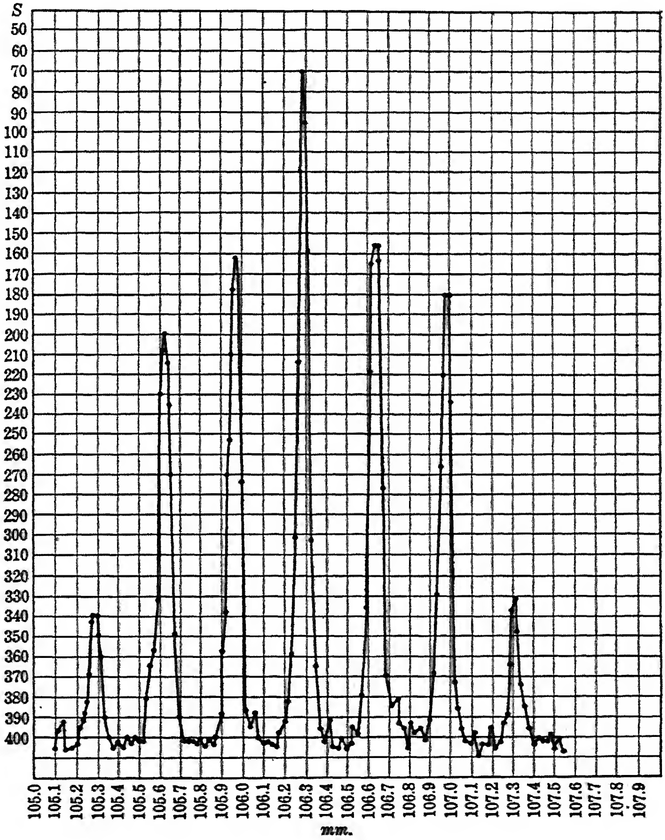

FIG. 77.

As an example of the effectiveness of the electro-photometer, we may mention the photometric study of a Zeeman splitting (zinc triplet photographed by G. Back); Figure 76 shows the original photograph, Figure 77 the photometric findings.

Another modification of photo-electric photometry has been elaborated for chemical investigations by H. von Halbak and H. Geigel (Zeit. f. Phys. Chem. **96**, 27, 1920), by using a rotating sector and reducing the cell to the function of indicator only.

CHAPTER XXI

SPECTROPHOTOMETRIC PROBLEMS

The oldest problem of spectrophotometry is the measurement of the energy distribution in the spectrum of a "temperature radiator." This problem was first undertaken by Langley in the investigation of the solar spectrum; later F. Paschen extended the investigation to artificial "radiators." A marked development in methods for measuring energy by means of linear bolometers and thermopyles followed and constituted the basis for the investigation of black body radiation and for the elaboration of the radiation laws of Wien and of Planck. The bolometric method consists in the measurement of the variation in resistance—by means of a wheatstone bridge—of a metallic strip heated by incident radiation. The bolometric method is adaptable likewise to absolute radiation measurements, according to the procedure of Kurlbaum, by producing the same temperature elevation by means of electric energy as obtained by direct radiation. The thermopyle, which likewise measures energy, may be utilized for absolute measurements, if the procedure suggested by Ångstrom—whose method subsequently was elaborated and improved by Paschen and Gerlach—is followed. According to this method, the thermo-elements are not illuminated directly by the radiation; but the radiation is incident upon a thin metallio strip placed in front of the temperature-sensitive soldered joints of the thermo-elements, and the temperature elevation of the strip is then measured; subsequently the strip is brought to the same temperature by means of electric energy.

Both the bolometric method as well as the thermo-electric method have been applied to the measurement of the energy distribution in the continuous spectrum of Roentgen rays. However, the very small amount of energy involved presents serious difficulties. This is especially true when there is question of measuring the energy of spectral lines. As a fact, Paschen succeeded by repeated refinements of his measuring methods in exploring intense infra-red line spectra by means of a thermopyle and a bolometer; the intensities of very prominent lines in the ultra-violet mercury spectrum likewise were measured thermo-electrically. Only one experiment is available in which the distribution of energy in the spectral lines of a series was measured by means of a thermopyle, viz.: the measurement by Jolly of the intensity of the first four members of the Balmer series of hydrogen. The sensitivity of thermo-electric methods of measurement is rarely sufficient to warrant their use in other spectral analytical problems. The direct measurement of energy is impossible likewise when measuring the energy distribution in the visible and the ultra-violet regions of the temperature radiation. The normal photometric and pyrometric methods are ordinarily employed in the region of the visible radiation of sufficient intensity, i.e., at a sufficiently high temperature of the radiator.

In all other cases recourse must be had to more sensitive methods which however do not record the magnitude of the radiation in energy units. These methods consequently must be standardized by comparison with the direct energy methods.

The photo-electric cell may be regarded as the most important and expedient instrument made available by the development of modern physics. This cell was discussed rather thoroughly in the previous chapter. It is equally applicable to the visible and the ultra-violet spectrum. However, few methods are available at present in which a radiation under investigation is measured directly by means of the photo-cell. In the majority of cases, the photo-cell is utilized to measure the "blackening" of photographic plates. In other words, the radiation under examination—e.g., the spectrum whose intensity distribution we are desirous of knowing—is photographed, and from the resulting blackening of the plate as measured by the photo-cell, we deduce the intensity of the incident radiation. Obviously, a knowledge of the laws governing the blackening of photographic plates is necessary. This constitutes the most important problem of photometric instruments, not only because of the exceedingly large number of their applications, but also because of the simplicity of the methods, since a large number, e.g., of spectral lines may be obtained simultaneously for intensity measurements by photography, the conditions governing the radiation source being easily maintained constant.

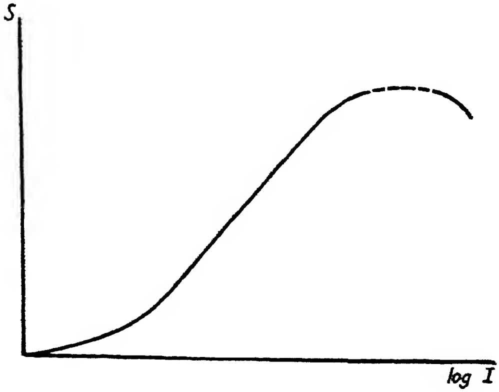

Fig. 78.

The "blackening" effect of a photographic plate may be interpreted either as the logarithm of the ratio of the light incident upon the "blackened" surface to the light transmitted through it; or as the logarithm of the ratio of the light transmitted through the blackened surface to the light transmitted by an "unblackened" portion of the plate, the intensity of the incident radiation being kept constant.

If the blackening of the photographic plate is measured as a function of the incident light, and the relationship plotted logarithmically (Fig. 78), we will obtain a curve which is linear for a limited range of intensity, but which will exhibit a maximum (saturation character) at stronger intensities and eventually indicate a decrease in blackening for still stronger intensity. A given blackening may therefore be obtained either by means of a small intensity over a long period of illumination, or by a stronger intensity coupled with a smaller illumination period. It was found that the Bunsen-Roscoe law of photochemistry—according to which a photochemical reaction depends merely upon the product of the intensity and the time of illumination, i.e., on the quantity of light—is not valid generally for the photographic plate, but may be replaced by Schwarzschild's law $S = Jt^n$, wherein the exponent n is usually smaller than 1 and a function of the wave-length of the incident (blackening) light; only for a few types of plates is $n = 1$. Using the data of Hurter and Driffeld, Stark has deduced a general law of "blackening," which may be formulated as

$$S = \log (K \cdot J^m t^n).$$

The following Figure 79 represents the dependence of blackening upon the logarithm of the illumination period; the marked similarity between this curve and that showing the dependence of blackening upon the logarithm of intensity (Fig. 78) is readily evident. The form of the curve is dependent upon wave-length in the visible region. This dependence becomes less marked the shorter the wave-length of the light and finally vanishes in the X-ray regions. This phase has already been given consideration in a previous chapter (XIV).

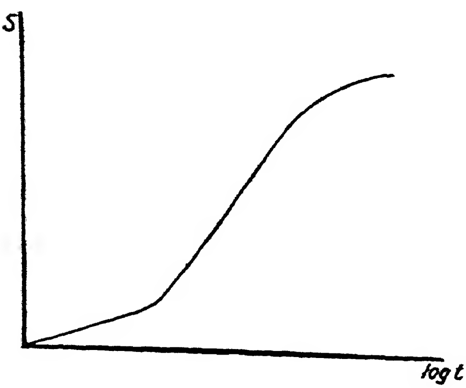

Fig. 79.

In carrying out absolute energy measurements by means of the photographic method, it is recommended that the "blackening" of the spectrum under investigation be compared with the "blackening" of a given spectrum whose absolute energy distribution is known. The simplest procedure would be the selection of the spectrum of a black body. However, the experimental production of black bodies of very high temperature—so that sufficient energy will be emitted in the short wave spectral region—is extremely difficult. On this account, electric incandescent lamps—such as tungsten-band-lamps—whose spectral energy distribution has been precisely measured, are adopted as normal light-sources. Such procedures, on the other hand, are not easy of attainment, since the law of blackening varies slightly from plate to plate and depends, in addition, upon the mode of development. Consequently, the spectrum under examination, the normal spectrum and the conditions governing the application of the law of blackening—i.e., the data necessary for the determination of the curves showing the relation of intensity to time—must all be photographed upon the same plate. The measurement of blackening may be carried out according to one of the methods described in the previous chapter. Still another manner of measuring blackening, proposed by Eggert, which very frequently is of great service, consists in counting the number of blackened silver bromide granules by means of a microscope: the number of blackened silver bromide molecules per unit of surface serves as a standard for comparisons.

We will cite here a few other problems for whose solution photometric methods are necessary. The problem of measuring the energies of various spectral lines, and of the intensity relationship of the individual components of a complex spectral line (multiplet), the measurement of the Zeeman-components, the intensity of the individual lines of a series spectrum are fundamental problems of interest to the theory of atomic and molecular structure. These topics were investigated by L. S. Ornstein (in Utrecht) and his students.

Another phase of this problem of the measurement of spectral intensity consists in a comparison of the intensity of spectral lines for the purpose of chemical quantitative analysis. Impurities present in a metal are evidenced by the appearance in the spectrum of the metal of the spectral lines of the impurities, even though the latter are present only to thousandths of a per cent. A quantitative analysis of the metal may be accomplished by comparative photometric measurements of the intensity of the spectral lines of the contaminations and of the spectral lines of the basic substances respectively. X-ray chemical analysis is carried out in a similar manner by comparing the intensity of the Roentgen spectral lines of the impurities with the intensity of the spectral lines of the main substance.

The measurement of astral temperatures presents still another problem. This is based upon a comparison of the "blackening" distribution in the astral spectrum with the corresponding distribution in the spectrum of a known terrestrial light source. Such measurements constitute the basis of the modern methods of the investigation of stars (Chap. XXX).

We may mention, finally, an entirely different method of radiation measurement. According to the quantum theory each radiation of a definite frequency is composed of a given number of light quanta $h\nu$, so that the radiation measured as energy E is equal to $E = n \cdot h\nu$. H. Geiger has proposed a method to count these quanta in the case of very weak radiations, i.e., for such radiations as emit only a few quanta in measurable time intervals. This method is based upon the fact that each quantum of a radiation incident upon a very fine metallic point produces upon the latter a specific photo-electric effect. The electron thus liberated may serve as an index of the number of quanta in the radiation. An important application of this method is found in the experiments of Bothe and Geiger which have been described in Chapter XVII.

CHAPTER XXII

INFRA-RED FREQUENCIES OF CHEMICAL RADICALS IN CRYSTALS

In connection with our discussion of the infra-red spectral region we emphasized the significance of reflection measurements on crystals as an aid in the exploring of crystal structure and data of more or less importance were presented. Among others, there was presented a table of "rest rays" of simple, binary, heteropolar crystals. In this chapter we shall treat of the reflection of salts in the infra-red, whose investigation has produced a definite coordination of reflection maxima to the individual constituents of such crystals, to the molecular groups or radicals of the chemical molecules. In addition, there were evidences of the influence due to the orientation of (linear) polarized light with respect to the crystal axes, "infra-red polychroism"; there also resulted certain views regarding the problem of the constitution of hydrated crystals, that is, of crystals that crystallize with "water of crystallization." These results may likewise prove very significant in understanding the actual chemical constitution of such crystal molecules. For, while the long wave infra-red frequencies—which were discussed at length elsewhere—are attributable to the reciprocal vibrations to one another of the divers polar constituents of the crystal molecule, the specific frequencies of the short wave infra-red (whose existence may be proved by selective absorption or selective reflection of the frequency in question) are due to the vibrations within the self-subsisting groups of the molecule. These latter vibrations are always characteristic of this grouping, the so-called "radical," it being immaterial whether the "radical" is present in the molecule as the electropositive or the electronegative constituent; nor are they influenced, except very slightly, by the mode of chemical combination of the radical.

An influence of this type is most in evidence in the fact that the spectral position of the vibration of salt-forming groups depends somewhat upon the metal-ion. However, there was no consistent evidence of regularity in effect; in fact, the influence of such positive constituents was not always in evidence. We shall, consequently, not enter deeply in the discussion of this problem even though this is of significance from the point of view of the atom theory, since the influence of the one radical upon the independent internal vibrations of the other is an indication of the deformation of the latter by means of the electric field of the former.

Not much need be said regarding methods. Most substances under examination cannot be obtained with well-defined, large surfaces as is desirable in view of the none too great radiation energy at our disposal, or of the none too great selective reflectivity. Therefore, to procure surfaces sufficiently extended for reflection experiment, very fine powder is compressed under several thousand atmospheres to plates[1] which may be polished; naturally, such a procedure destroys all orientation of the crystal axes. A second method consists in assembling (in the manner of a mosaic) small but well-formed crystals, proper attention being given to the orientation of the respective surfaces: thus the resulting plates may then be cut and polished. This method was adopted by Cl. Schaefer and M. Schubert in their investigations which will be described later.

In order to register the reflection curves, use is made of a mirror spectrometer with a quartz, fluorspar or sylvite prism, whose dispersion curves in this range are very well known. Absorption curves may also be obtained in place of the reflection curves. This method was elaborated by O. Reinkober.[2] On account of the strong absorption, these layers must be very thin; they may be obtained in uniform, serviceable layers of 1–2 μ thickness by sublimation or vaporization. In return, however, a marked advantage accrues since the

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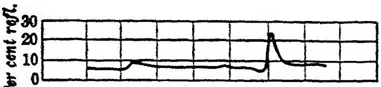
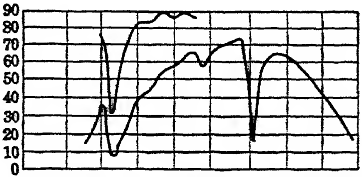
[1] First carried out by H. Rubens.

[2] O. Reinkober, Zeitschr. f. Phys. 5, 192 (1921).

results are not vitiated by surfaces of molecular thickness that may arise because of corrosion, lack of finish, etc.; furthermore, the adjustment of the absorption method is much simpler, as a consequence of which measurements on changeable substances may the more rapidly be carried out. Strongly hygroscopic substances may be enclosed between two plates and thus withdrawn from the action of moist air. Figure 80 presents a measurement made by Reinkober on ammonium chloride, curve *A* showing the absorption data, and curve *R*, the reflection data. The advantage of the absorption curve is readily perceptible, the method being more exact. The thickness of the layer was of the order 1–2 μ. For numerical data refer to the table marked "Ammonium Halides."



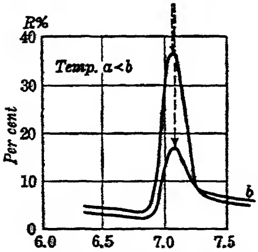
Reflection curve of the same material



NH_4Cl
Absorption: Layers of two different thicknesses

FIG. 80.

Attention may be drawn, also, to the "temperature coefficient" of the specific vibration, determined by O. Reinkober[3] for the ammonium salts, in which he obtained more sharply defined results than the previously determined values of Rubens and Hertz.[4] Generally, a decrease in reflectivity sets in with increasing temperature accompanied by a simultaneous broadening of the reflection maxima and its displacement toward greater wave-lengths (Fig. 81). The appearance of weak secondary maxima at low temperature only may be due to the fact that they are marked at higher temperatures of the crystal because of the width of the primary maximum



Temperature-coefficient of specific vibration (NH_4Cl)

FIG. 81.

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[3] O. Reinkober, Zeitschr. f. Physik 3, 318 (1920).

[4] H. Rubens and G. Hertz, Berl. Ber. 1912, 256. Measurements made on quartz and calcite in short-wave regions.

and because of a simultaneous decrease in intensity of reflection at the higher temperatures. The phenomenon is very familiar, in fact, in the increasing fineness of absorption bands in colored crystals with decreasing temperature.

Whether we are here concerned with a "pressure effect" or with some phenomenon based on the nature of the internal vibration—possibly susceptible of a quantum interpretation—is a question that cannot be decided at this point. By means of absorption the molecules are transposed into higher energy states. The absorbed energy, however, is not totally reemitted (reflected), but a portion of it is transformed into kinetic energy, that is, is lost as radiation energy of the characteristic frequency. The intensities of reflection (taken from Reinkober's measurements) are inversely proportional to the square of the absolute temperature.

We will now take up, seriatim, the reflection maxima of various substances, arranging them according to corresponding radicals in the crystal molecule.

Reflection of Ordinary Light

All wave-length data are given in μ

SULPHATE

$SO_4^{=}$ Group

Simple Sulphate	Wave-length			Remarks
Lithium sulphate.....	3	8.76	15.32	$1H_2O$
Sodium "	—	8.72	16.08	Water free
Potassium "	—	8.82	15.97	
Copper "	3	9.20	15.88	$5H_2O$
Beryllium "	3	8.82	16.04	$5H_2O$; second max. 9.08 μ
Calcium * "	3	8.74	14.84	$2H_2O$; " " 8.62 μ (very weak)
Strontium "	—	8.84	15.75	Small elevation at 8.35 μ
Barium "	—	8.91	15.8	
Cadmium "	3	9.02	15.96	$8/3H_2O$
Nickel "	3	9.01	15.74	6 molecules H_2O

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* Gypsum has a very high reflection capacity (70 per cent), and therefore is adapted for isolation of "rest rays." In earlier measurements, however, the complexity of the first maximum was always overlooked. See below for details (reflexion in polarized light).

Isomorphous Mixtures of the Free Sulphates
(Chemical nature not quite clear)

Lithium-potassium sulphate	8.72	15.78	
Sodium-potassium sulphate	9.03	16.15	Water free, no max. for 3 μ
Potassium-ammonium sulphate	8.82	16.08	

Isotropic Double Sulphate (Alums)

Chrom-alum of	Potassium	Rubidium	Thallium	Ammonium
λ in μ	9.03 16.44	9.04 16.44	9.06 16.44	9.10 16.32

Aluminum Alum of	Thallium	Caesium	Potassium	Ammonium
λ in μ	9.06 16.48	9.06 16.52	8.96 16.74	9.04 16.60

In addition, all show weak maxima for 3 μ and for 14 μ.

Furthermore, the corresponding potassium double salts of

Mg	Co	Zn	Mn	Ni	Cu
8.91	9.03	9.05	8.74 9.28	8.89	9.10
15.80	15.90	16.02	16.24 16.42	15.84	16.40

all crystallize with 6 molecules of water and show a maximum of reflection at 3 μ. The anisotropic double salts show, just as do the alums, a weakly placed maximum at 14 μ, as is evident from Figure 82, which is also in evidence in the

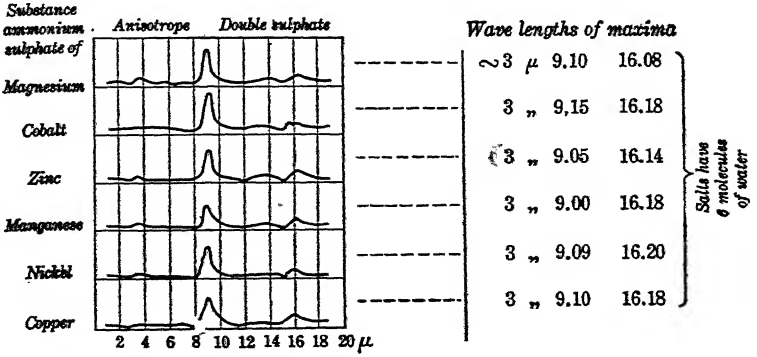

FIG. 82.

reflection curves of $NiSO_4$, $CaSO_4$, and $BaSO_4$, all of which are simple sulphates.

In summarizing these data we may conclude: all sulphates show at 9 μ and at 16 μ the reflection maxima characteristic of, and peculiar to, the $SO_4^=$ ion. Since the positions of these maxima are influenced but very slightly by the anion (although this may vary markedly) and since they make their appearance at the same positions for complex salts as well, they cannot be attributed to vibrations between anion and cation (= $SO_4^=$ radical). They give evidence rather of the internal vibration frequencies of the radicals, whose slight change with the nature of the anion and the mode of chemical combination is readily understandable as the result of exterior forces operative at relatively great distance to effect an inner change within the radical. The maxima observed for 3 μ and for 14 μ, respectively, are obtained only for hydrated crystals and are therefore identical with the reflection maxima of water. This phase will receive fuller discussion in a later section. (See the rôle of water of crystallization, p. 345.)

SELENATES

Group $(SeO_4)^=$

Simple Selenates

Potassium	Selenate	11.20	Anhydrous
Manganese		11.36	
Nickel	"	11.44	Hydrated crystals all show the reflection maxima of water
Copper	"	11.52	
Zinc	"	11.44	
Cadmium	"	11.44	
$(SeO_4)_2Na_3Li$	"	11.38	

Double Selenates

	λ	
$(SeO_4)_2Mg(NH_4)_2 \cdot 6H_2O$	11.18 μ; 11.36 μ	
" $Mn(NH_4)_2 \cdot 6H_2O$	11.44 μ; 11.68 μ	
" $Ni(NH_4)_2 \cdot 6H_2O$	11.18 μ; 11.42 μ	All show in addition the maxima for water
" $Co(NH_4)_2 \cdot 6H_2O$	11.48 μ	
" $NiK_2 \cdot 6H_2O$	11.16 μ; 11.52 μ	
" $ZnK_2 \cdot 6H_2O$	11.22 μ; 11.5 μ	

CHROMATES

Potassium chromate, K_2CrO_4	11.16	
Sodium-potassium chromate	11.2	(Very strong, 80 per cent refl.)
Magnesium-ammonium chromate, $Mg(CrO_4)_2.(NH_4)_2.6H_2O$	11.3	11.42, also H_2O and NH_4 refl.

What has been said regarding sulphates applies also to the selenates and to the chromates: they possess characteristic frequencies that are peculiar to the SeO_4 and CrO_4 radicals respectively.

CARBONATES [5]

In addition to a large number of uni- and di-axial carbonates, a regular carbonate and an organic carbonate were investigated. To anticipate the results: all carbonates possess three characteristic reflection maxima, respectively, at 6.5, 11.5 and 14.5 μ, which are entirely independent of the crystal form.

Regular carbonate..........	Northupit, $MgCO_3$, Na_2CO_3, NaCl	6.82	11.46	14.14
Uni-axial..................	Rhodochrosite	6.76	11.38	14.04
	Siderite	6.77	11.53	13.54
	Smithsonite	6.78	11.44	13.92
	Magnesite	6.69	11.25	13.78
	Calcite	6.56[6]	11.38	14.16
	Dolomit ($MgCO_3.CaCO_3$)	6.90[7]	11.45	14.70
Di-axial carbonates..........	Aragonite (Ca)	6.64[6]	11.54	14.40
	Strontianite (Sr)	6.78	11.62	14.28
	Witherite	6.85	11.61	14.48
				14.92
	Cerusite (Pb)	7.06	12.00	15.20
	Sodium Carbonate	7.00	11.48	14.56
Organic carbonate (uni-axial).	Guanidine Carbonate	7.34[8]	12.38	15.10
Basic carbonate.............	Malachite, $CO_3(CuOH)_2$ 6.64 7.16	9.64[9]		
		11.56	12.14	13.32
	Azurite, $(CO_3)_2Cu(CuOH)_2$ 7.00	10.54	11.92	14.16

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[5] Cl. Schaefer and M. Schubert, Ann. d. Phys. 50, 283 (1916).

[6] First maximum is complex.

[7] Exactly like the simple carbonates.

[8] Very weak reflection, double refraction; also very small (Relationship?).

[9] Appearance of a new characteristic reflexion maximum characteristic of the basic salt.

NITRATES[10]

Sodium nitrate, $NaNO_3$	7.12	12.04	14.44	
Potassium nitrate	7.18	12.25	15.14	
Rubidium nitrate	7.24	12.32	15.24	
Strontium nitrate, $Sr(NO_3)_2$	7.28	12.36	15.36	
Barium nitrate	7.3	13.74	15.58	
Lead nitrate	7.72	13.94	15.92	
Mercury nitrate, $HgNO_3.1H_2O$	8.06	12.50	15.92	In addition, at about 3 and 6 (water) and at 10.08

In ordinarily light nitrates exhibit three frequencies just as do the carbonates.

The fourth maximum arising in the case of mercury nitrate seems to contradict the statement that three and only three maxima are ascribable to the nitrate radical. It was subsequently demonstrated, however, that immediately upon polishing the surface of the nitrate it was transposed into a basic nitrate. The fourth maximum may be attributed, therefore, to the basic nitrate; in other words, we have here an effect similar to that shown by the basic carbonates (malachite and azurite), viz.: the appearance of a new reflection maximum between the first and the second normal maxima.

CHLORATES, BROMATES, IODATES

Substance	Crystal Form	Reflection Maxima	
$NaClO_3$	regular	10.04	16.04
$KClO_3$	monoclinic	10.12	16.22
$AgClO_3$	tetragonal	10.76	16.38
$Ba(ClO_3)_2H_2O$	monoclinic prismatic	10.24	19.6
$NaBrO_3$	regular	15.24	-
$AgBrO_3$	tetragonal	12.62	13.10
$Cd(BrO_3)_2H_2O$	rhombic	12.32	13.20
$Ba(BrO_3)_2H_2O$	monoclinic	12.32	12.64
KIO_3	regular	12.48	13.16

Here we again have similar results. The data of this table emphasize especially the complete independence of the crystal form on the part of the infra-red reflection maxima.

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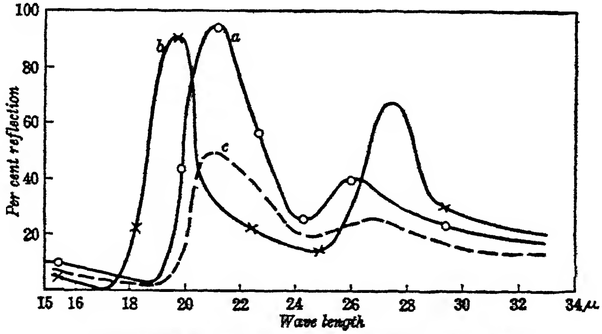
[10] Cl. Schaefer and M. Schubert, Ann. d. Phys. 58, 577 (1918); A. H. Pfund, Phys. Rev. 24, 19 (1906).

SILICON DIOXIDE

The optical behavior of quartz has been subjected to many and very accurate investigations. Silicon dioxide, however, occurs in various modifications and may also be prepared in definite forms, e.g., quartz-glass. It would be of interest, therefore, not only to compare the deportment of these modifications with respect to one another, but also to make a comparative study of the Roentgen analysis [11] of such SiO_2-bodies and of the corresponding behavior in the infra-red. The following figure depicts the data obtained from such an investigation by Cl. Schaefer and M. Schubert.[12]



Reflection measurements on quartz according to Liebisch - Rubens
(a) Quartz ordinary ray
(a) Quartz extraordinary ray
(c) Quartz amorphous (quartz glass)

FIG. 83.

In this connection, it is of interest likewise to compare the behavior of quartz and other silicon dioxide modifications toward still greater wave-lengths. Available data for such a comparison are contained in the two researches of Liebisch and Rubens. Let us first direct our attention to the continuous curve marked with the little circlets (Fig. 83). This curve represents the reflection dispersion of an ordinary ray by crystallized quartz. The curve, marked with crosses, designates a corresponding result for the extraordinary ray.

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[11] Carried out by Kyropoulos, Zeitschr. f. angew. Chem. 99, 197 (1917).

[12] Cl. Schaefer and M. Schubert, Zeitschr. f. Phys. 7, 313 (1921).

Quartz-glass—as indicated by the broken curve—gives an entirely different effect. To be sure, the maxima lie at approximately the same wave-lengths, but by no means are they the average values of the two rays obtained with the crystalline SiO_2-form, and, furthermore, the extent of reflection is always much smaller. Amorphous quartz likewise shows a small reflectivity in the short wave region (see Fig. 84) but contrary to opal it shows a fine structure of the reflection bands. This contrast becomes still more accentuated in the long wave reflection range of the opal; no SiO_2 modification exhibits here a reflection maximum.

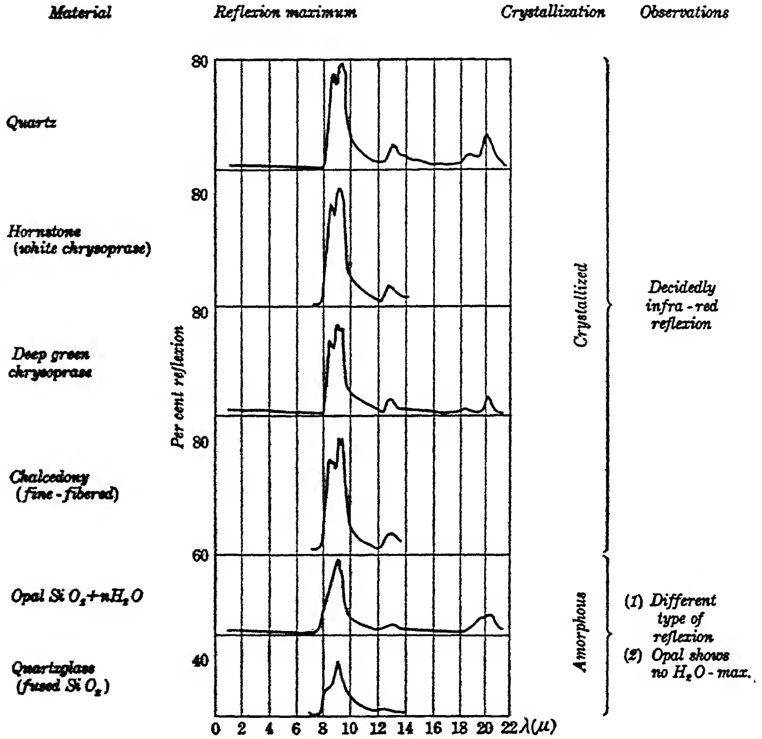

FIG. 84.

Below are listed all the reflection maxima obtained from crystalline quartz:

(*a*) Electr. vector parallel to axis	8.50	8.70	8.90	9.05	12.87	19.7	27.5
(*b*) " " perpendicular to axis	8.50	—	8.90	9.05	12.52	21.0	26.0

Of these, the first are contained in Figure 84, and the two last in Figure 83.

AMMONIUM HALIDES [13]

	Abs.	Refl.	Abs.	Refl.	Abs.	Refl.	Abs.	Refl.	Abs.	Refl.	Abs.	Refl.
NH_4F	3.5	—	—	—	4.5	—	5.0	—	6.0?	—	6.69	6.69
NH_4Cl	3.24	3.2	3.5	—	4.25	—	4.95	—	5.66*	5.85	7.07	7.07
NH_4Br	3.22	3.2	—	—	4.3	—	4.9	—	5.9	5.9	7.10	7.11
NH_4I	3.22	3.2	—	—	4.27	—	5.0?	—	6.0?	—	7.15	7.18

* Difference from 0.2 μ is real. Explanation?

These experiments yielded the same results as all the others; they indicate—which may be emphasized especially—that the inner frequencies belong to each molecular grouping, even if this grouping constitutes, as in the case of ammonium salts, the positive radical of the salt. In the case of the nitrate and the sulphate, we have, in addition to the specific (NH_4)-vibrations, the vibrations peculiar to the NO_3 and the SO_4 radicals respectively.

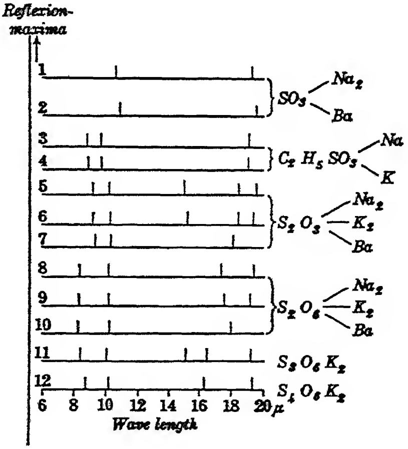

FIG. 85.

OTHER (S_xO_y)-CRYSTALS

Figure 85 represents synoptically the results of twelve experiments carried out by V. J. Sihvonen. Abscissæ designate wave-lengths, and ordinates the—approximate—intensity of reflection of the individual measurements. The data are grouped according to the character of the negative radical. It is obvious that the SO_3 group, the sulphite radical, exhibits a strong and a weak reflection analogously to the sulphate

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[13] O. Reinkober, Zeitschr. f. Phys. 3, 4 (1920); 5, 192 (1921).

ion; the more complex negative radicals, S_2O_3, S_2O_6, etc., have numerous reflection maxima, and therefore a larger number of inner vibrations. In every instance there is evident a slight dependence of reflection wave-length upon the nature of the metal-ion, but this does not show any definite regularities.

A word more regarding the existence of "harmonics" in crystals, a problem recently treated experimentally by Schafer and Thomas. Such vibrations may be expected if the vibrations are not harmonic. As a matter of fact such vibrations have already been observed, e.g., in the investigation of $SrSO_4$ by the absorption method.

	Observed	Calculated Frequency Ratio
Celestine: Fundamental frequency	8.35 μ; 9.05 μ	1
I Octave	4.5 μ	1 : 2
Duodecimo	3 μ	1 : 3
II Octave	2.3 μ	1 : 4

An exact determination of these octave vibrations would aid in solving the problem of their—insignificant—displacement ("discord") by the electric fields in the crystals.

REFLECTION POLARIZED LIGHT

Infra-red Pleochroism

It may be surmised from the form of many reflection maxima that they do not consist of a single homogeneous reflection but are composed rather of several reflections which overlap so closely (for example, strontium sulphate, Fig. 86*b*) that they cannot be resolved into their components by the spectral apparatus employed. This conjecture is strengthened by the splitting of the maximum in certain cases (e.g., beryllium sulphate, Fig. 86*a*), which is indicative of the complexity of the reflection. Complexity is likewise evident in the pronounced unsymmetrical maximum exhibited by strontium sulphate (Fig. 86*b*). Schaefer and Schubert accordingly undertook a series of experiments to determine whether a relation existed between the position of the maximum and the orientation of the polarization plane with respect to the optical axes of the reflecting crystal.[14] Using polarized light (selenium polarizer) and taking into account the orientation of the crystal, these observers found the same result for all cases tested: regular crystals show a single maximum which is independent of the orientation; uni-axial crystals show dichroism, and biaxial crystals show trichroism. We shall cite a few examples: thus, uni-axial sodium-potassium sulphate exhibits maxima at 9 μ and at 16 μ (Fig. 87). These crystals show other interesting characteristics. Thus, an anisotropy is observed not only for the frequencies, but likewise with respect to the damping of the vibrations, for the absolute values of $R//$ and of $R\perp$ to the optical axes are not equal. Furthermore the curves overlap so that there are certain wave-lengths at which the crystal is isotropic and certain points in which the sign of the double refraction is reversed.

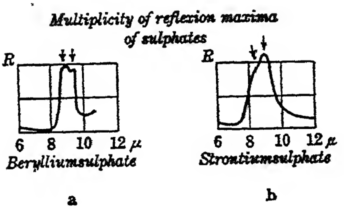

FIG. 86.

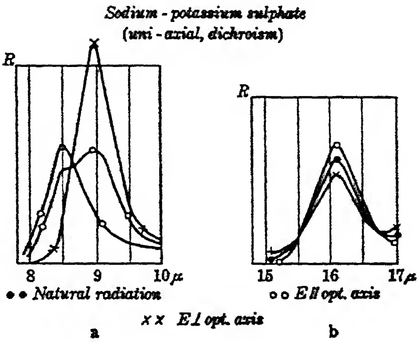

FIG. 87.

Bi-axial crystals exhibit a splitting up of the infra-red reflection maximum into three characteristic vibrations, as is evident from Figure 88 which presents the maximum for celestite at 9 μ.

This phenomenon also explains the remarkable result obtained by M. Randall when measuring the wave-lengths of

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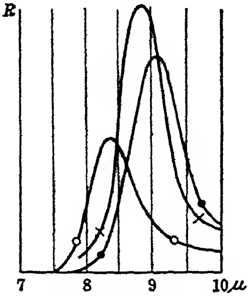
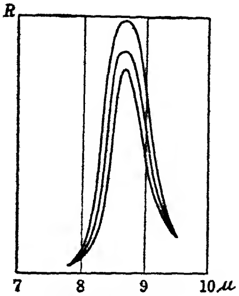
[14] Analogous experiments are due also to Nyswander, Phys. Rev. 28, 291 (1909) [calcite and aragonite]; also to O. Reinkober, Ann. d. Phys. 34, 345 (1911) [tourmaline and quartz].

the "rest rays" of gypsum; he obtained values for the wavelengths of maximum reflection which depended somewhat upon the measurement method. Figure 89 shows the trichroism of gypsum; the position of the maximum will depend upon the value of the partial polarization of the radiation reflected, adjustments being made with respect to the center of gravity only. Partial polarization is unavoided when working with prism-spectroscopes.



○○E∥c ●●E∥b ××E∥a
Celestin

FIG. 88.



Trichroism of gypsum
Upper curve E∥c
Middle curve natural radiation
Low curve E∥a
(E∥b, not measured)

FIG. 89.

Exactly the same result is observed for the carbonates, excepting that the form differs somewhat in details. The other uni-axial carbonates of the calcite type examined by polarized light show that of the three measured maxima, the first (6.5 μ) and the third (14.5 μ) are due to the ordinary ray (electric vector perpendicular to the optical axis), whereas the second is attributable to the extraordinary ray (parallel to optical axis). Figure 90 takes siderite ($FeCO_3$) as an example. Bi-axial crystals exhibit an analogous behavior. The middle reflection maximum corresponds to the specific vibrations parallel to the a-axis. The two exterior curves result from reflection parallel to the b- and c-axes, respectively, each curve showing two distinct maxima. Figure 91 depicts the behavior common to all (cerussite, $PbCO_3$, may be taken as an example for the first and second maxima).

Schaefer and Schubert refer to an analogy of optical behavior: just as the optical refraction indices, measured parallel to the b- and c-axes (i.e., the medium and the largest components), differ but slightly from one another, and do not lie close to the index measured parallel to the a-axis (the smallest exponent), so also do the infra-red frequencies of the b- and the c-axes lie close together but separated widely from that of the a-axis.

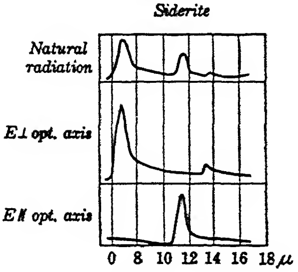


Fig. 90.

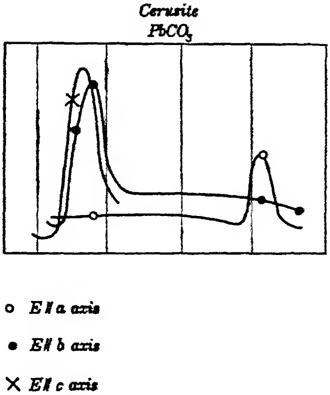


Fig. 91.

Sodium saltpeter, potassium saltpeter and rubidium nitrate are doubly refractive, as is well known. In polarized light there were not found for sodium nitrate individual maxima for the ordinary and the extraordinary rays but merely a splitting up of the maxima. Analogous results were noted for the other two substances mentioned. In the case of bi-axial potassium saltpeter the maximum breaks up into three components. The following wave-lengths may be listed:

Sodium nitrate (sodium saltpeter)	Unpol. light.............	7.12 μ	12.04 μ
	Pol. light................	7.24 μ	11.86 μ
		7.04 μ	12.00 μ
Potassium nitrate (potassium saltpeter).................		7.25 μ	parallel to a-axis[15]
		7.21 μ	" " b- "
		7.12 μ	" " c- "

[15] Parallel to axes a, b, c = smallest, medium and largest refraction index.

This result is especially remarkable since sodium saltpeter and calcite, on the one hand, and potassium saltpeter and aragonite on the other hand, not only have analogous optical behaviors but are characterized (according to Bragg) by the same crystal grating. Although this conforms to the isomorphy of the substances in question, the behavior noted in the infra-red is markedly different, the difference being due, undoubtedly, to unknown but essential differences in the structure of the nitrate and carbonate, which are not detectable at present by the X-ray analysis of crystals. For at present there is no justification for us to abandon the explanation of reflection maxima as inner frequencies peculiar to a definite grouping, in this instance the NO_3 and the CO_3 radicals. It would rather be of utmost interest to correlate, more than has been attempted heretofore, X-ray and infra-red ray analysis, as recently undertaken by St. v. d. Lingen in his investigations on liquid crystals (for details see p. 359) and by Cl. Schaefer and M. Schubert in their discussion on the SiO_2 reflections (see above).

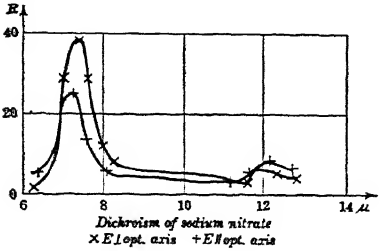


FIG. 92.

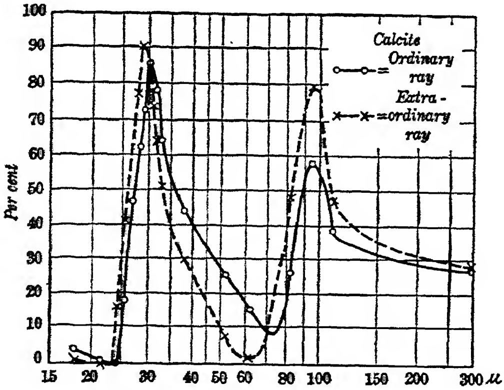


FIG. 93.

Analogous experiments were carried out by Liebisch and Rubens[16] on double refracting crystals in the long wave infra-red. Monochromatic radiation dispersed in the continuous spectrum by means of a prism or grating could be utilized to some extent only in the first part of this spectral region. Rest ray arrangements were used in the long waved region to produce the individual wave ranges whose wave-lengths have already been given on p. 282. It is therefore not possible to change the wave-lengths continuously in this spectral range or to calculate the probability that there were more specific vibrations than actually observed. The reflection plates employed were either large plates orientated to the crystallographic axes or mosaics composed of small orientated surfaces. The determination of the reflective power of the ordinary and the extraordinary rays may also be carried out with natural radiation by measuring the reflectivity of two plates, one cut parallel to the optical axis and the other cut perpendicular to the axis. The latter is the reflectivity of the ordinary ray and may be designated by R. The reflectivity of the plate cut parallel to its axis is $R_p = \frac{1}{2}(R_0 + R_e)$, from which the reflectivity of the extraordinary ray may be computed as $R_e = 2R_p - R_s$.

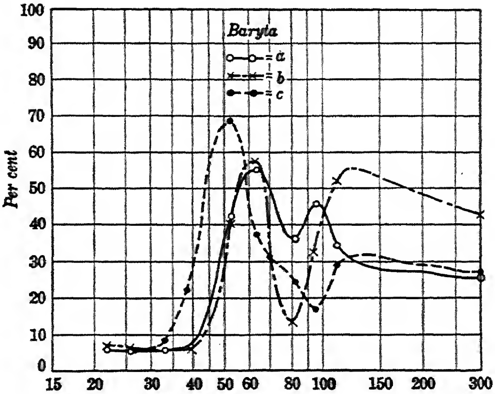


FIG. 94.

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[16] Th. Liebisch and H. Rubens, Berl. Ber. 1919, 198 (1st com.), 876 (2d com.).

We shall refrain from a restatement of the very comprehensive experimental data and shall confine ourselves merely to Figures 93–95[17] which represent the very fine results obtained for calcite (uni-axial) and with barite ($BaSO_4$) and celestite ($SrSO_4$) (both bi-axial). No evidence was obtainable of a relation between the short wave infra-red and the long wave vibrations, and, particularly, no evidence of a similarity of position of the long wave reflection maxima for equal anions and cations in the crystal. We shall give a few data obtained for salts with the NO_3 group and the NH_4 group of long wave specific vibrations:

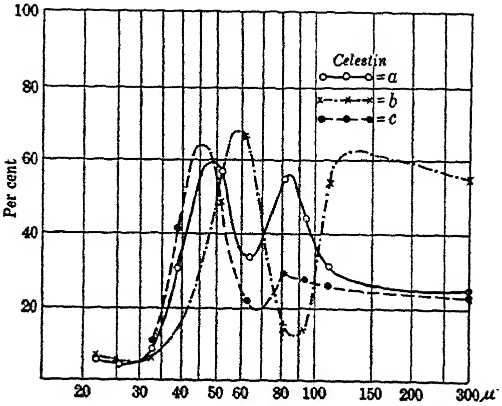

FIG. 95.

NO_3 Group		NH_4 Group	
$NaNO_3$	46 μ 110 μ	NH_4Cl	51.5 μ
$Pb(NO_3)_2$	79 μ	NH_4Br	59.5 μ

The specific vibrations thus established by Liebisch and Rubens in the long wave range may be explained as are the rest rays of the simple regular binary salts. The marked increase of wave-length (decrease of frequency with increasing atomic weight of the positive radical is particularly notable, to which fact attention has been directed in a previous section (Table of Rest Rays, p. 282)).

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[17] The scale of wave-lengths is logarithmic.

It is worthy of note, also, in this connection, that the "yield" of reflected energy is throughout very much larger for the long wave vibrations than for the short wave vibration; for the former, this frequently amounts to 90 per cent. Although we are not in a position to offer an explanation for this at present, we nevertheless would refer again to the observations made in regard to the temperature coefficients. It is evident, without further explanation, that disturbances are considerably greater, in the interval between the absorption of energy and its subsequent disengagement, within the closely packed space of the radical than within the crystal gratings due to the coarse-meshed structure of the latter in comparison to the diameters of ions (and radicals). The "anisotropy of dampings" to which Schaefer and Schubert (see above) have made reference in the short wave region of specific vibrations, is found also in the specific vibrations of the ions with respect to one another.

Another essential observation must be made here. It appears self-evident that the long wave vibrations should present polychroism characteristic of grating symmetry but it is a fundamental observation for a complete theory of crystal structure that the internal vibrations within the radicals should also present in the described polychroism the symmetry of the grating. It is clear that the analysis of the infra-red may in certain cases lead to a much more complete elucidation than Roentgen analysis.

With regard to all the theoretical questions involved we can do no more than refer to the comprehensive studies of Brester.[18]

THE RÔLE OF WATER OF CRYSTALLIZATION

Mention has already been made in several previous sections that all hydrated crystals exhibit the typical reflection maxima of water even though these are slightly displaced in their respective positions. Of especial interest in this regard is the determination, due to the extremely

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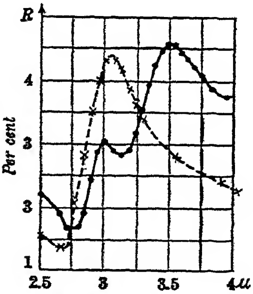
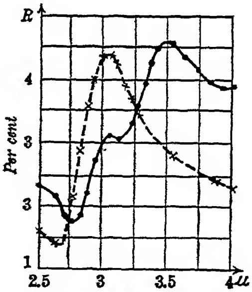
[18] Brester, Diss. Utrecht; Zeitschr. f. Physik 24 (1924).

careful and comprehensive experiments of Cl. Schaefer [19] and his coworkers, M. Schubert and K. Brieger,[20] that the reflection maxima at 3.2 μ and 6.5 μ in double refracting crystals are resolved, respectively, into two and three maxima in polarized light of definite orientation to the principal axes of the crystals, analogous to the results obtained for other groups, viz.: CO_3, NO_3, SO_4, etc. We must conclude, necessarily therefore, that a very definite rôle must be ascribed to water of crystallization as far as the crystal structure of hydrated crystals is concerned; for it deports itself exactly as an essential constituent. Two years after this discovery, Vegard and Schjelderup [21] gave an account of the disposition of the water of crystallization in the crystal structure of the alums which they had investigated according to Bragg's method.



Splitting of 3μ-reflexion maximum of water of crystallization in potassium alum (•), and of free water (x)

FIG. 96.



The same for thallium alum (•), and free water (x)

FIG. 97.

A few examples are given in Figures 96–99. In isotropic crystals, water is likewise isotropic; one observes merely a slightly displaced maximum toward the long wave end of the spectrum. The alums, also isotropic, show a doubling of the two reflection maxima at 3.2 μ and 6.5 μ (Fig. 99). They

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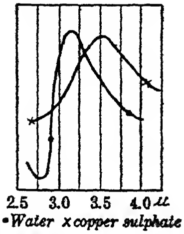
[19] Cl. Schaefer and M. Schubert, Ann. d. Phys. 50, 339 (1916).

[20] K. Brieger, Ann. d. Phys. 57, 287 (1918).

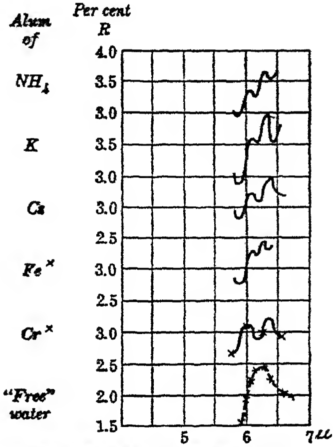
[21] L. Vegard and O. Schjelderup, Ann. 54, 146 (1917); 58, 291 (1919): Reply to above by Cl. Schaefer and M. Schubert, Ann. d. Phys. 55, 397 (1918); 59, 583 (1919).

all contain 12 molecules of water. At present this phenomenon can be explained only in an hypothetical way; an attempt at such an explanation was proposed in connection with Werner's association of water of crystallization to double molecules. Since free water itself, however, is considerably associated according to Nernst, it is not quite intelligible why this double-maximum is not in evidence in the reflectivity of the water itself: as a fact such a splitting of the water maximum was never observed, not even by K. Brieger, who measured the reflection of water with the same apparatus which she had employed for the study of crystal hydrates. It is possible that a partition of the 12 H_2O molecules into two groups of 6 H_2O molecules each takes place. Other hydrated crystals do not exhibit such a "double" maximum. In Figure 100 and Figure 101 are shown the dichroism and the trichroism of water respectively in uni-axial crystals and bi-axial crystals.



Displacement of reflexion maximum of "free" water and water of crystallization

Fig. 98.

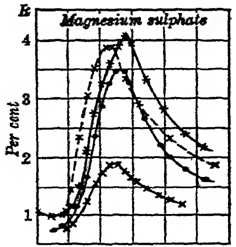


Splitting of 6μ-reflexion maximum of water of crystallization in alums.
× Ammonium alum

Fig. 99.

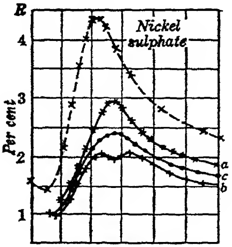
The interesting problem as to the manner in which water is combined in the zeoliths has not yet been investigated. K. Brieger had available only one regular zeolith, analcime

($Na_4Al_4Si_8O_{24}.4H_2O$), which exhibited the first reflection maximum of water with a slight displacement toward the short wave end (maximum found at 2.99 μ—probably the result of the chemical combination of the water (?)). Study of double refracting zeoliths may help decide whether or not the water is part of the space lattice.



Trichroism of water of crystallization
Magnesium sulphate ×*E*∥*a*
•*E*∥*b*
×*"Free" water* ✱*E*∥*c*

FIG. 100.



Dichroism of water of crystallization in nickel sulphate (uniaxial)
✱*Natural light* +*E*∥*opt. axis*
"Free" water ✱*E*⊥*opt. axis*

FIG. 101.

A second instance in which water shows an anomalous behavior in solid bodies is had in the opal. Opal is a silicic acid-gel of high water content, and yet no trace of a "water maximum" is observable in the infra-red reflection spectrum. Explanation for this phenomenon is still lacking. We can only confirm the absence of a crystal lattice in the opal and consequently there can be no question of water of crystallization.

CHAPTER XXIII

STRUCTURE ANALYSIS BY MEANS OF X-RAY

It is generally known, at present, that one of the most important applications of X-rays consists in the explanation by their means of the "fine-structure" of matter. By reversing Laue's conception—the utilization of the lattice structure of crystals as diffraction grating for X-ray spectroscopy—we can determine, from the known wave-lengths of the X-rays utilized, the lattice constants of crystals, their crystal structure, and, finally, the construction of crystals from their constituent atoms or molecular groups comprising the molecules.

We shall not enter into an exhaustive discussion of the more general investigations of this subject. Many crystal structures have been ascertained,[1] and the crystal form of nearly all the elements made known. It is likewise known that almost all bodies, ordinarily characterized as "amorphous," in reality are crystalline in structure. Many important organic substances as cellulose have been examined and the physical structure of their fiber explained. Metallography is at present beginning to explain solid phenomena. However, a still greater number of problems confronts us and these all await solution. In this connection, we may refer to the X-ray investigation of the experiments of Biltz and Hüttig which are very noteworthy in regard to the theory of molecular structure; the results of these experiments, although very clear and definite chemically, are hardly intelligible at present from a physical point of view (according to Kossel's theory).

We shall confine ourselves in the following pages to a discussion of a few problems of a special character, whose solution was made possible with the help of X-rays; we will,

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[1] Resumé in Roth-Scheel's "Atomic Constants" (Springer, 1923).

however, preface this discussion with a few preliminary remarks regarding the more recent progress in methods.

Apparatus

X-rays have been prepared in various forms for spectroscopic purposes and for crystal photography. The essential factor in the construction of these tubes is capacity; further, they must possess easily removable and replaceable anticathodes; "windows" (screens) for the emergence of the X-rays without appreciable loss by absorption; the distance from the anticathode to the screen must be as small as possible in order to utilize as much as possible of the radiation. The extent of their utility is exclusively a question of correct cooling of the anticathode inasmuch as the tubes must be loaded very heavily for extensive periods in order to procure proper intensity of radiation. This is necessary since rather long wave-lengths (of the order 1 Å.), i.e., low potentials (below 30,000 volts), are employed. The metallic tubes constructed by A. Hadding[2] have found extensive use, e.g., the type devised by A. Schmidt, the mechanician of the Frankfurt Institute. O. Pauli[3] proposes a tube-end which obviates the use of the expensive insulator of Hadding's tubes.

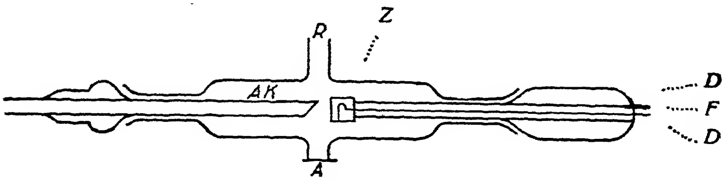

FIG. 102.

An advance in the tube construction is had in the tubes made by F. Kirchner.[4] This tube (see Fig. 102) makes use of an incandescent cathode (as did Hadding's tube) and is constructed of Jena glass, 12 cm. long and 35 mm. wide

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[2] A. Hadding, Zeitschr. f. Phys. 3 (1920).

[3] Described by O. Pauli, Zeitschr. f. Kristallographie, etc. 56 [6], 591 (1921).

[4] F. Kirchner, Diss. Jena (1922).

(manufactured by O. Schott and Gen). The ground-in extension tubes (7 cm. long) support the incandescent cathode and the anticathode respectively. *A* is a screen for the emergence of the rays, and *R* leads to a pump. The incandescent filament is a U-shaped tungsten wire 0.2 mm. thick contained in a box *Z* of molybdenum (10 mm. edge) in order to "center" the cathode rays. The molybdenum box is held in place by the two molybdenum wires *DD* fused in glass. The current enters the filament at *F* and returns by way of the molybdenum box *Z* and one of the wires to the source of the current. The tube is operated with 500-cycle alternating current without a rectifier but with a transformer. The potential varies according to the metal used as the anticathode (about twice the minimum potential of the K-series). The current density may be 30–40 milliamperes for long intervals and 60 milliamperes for shorter periods.

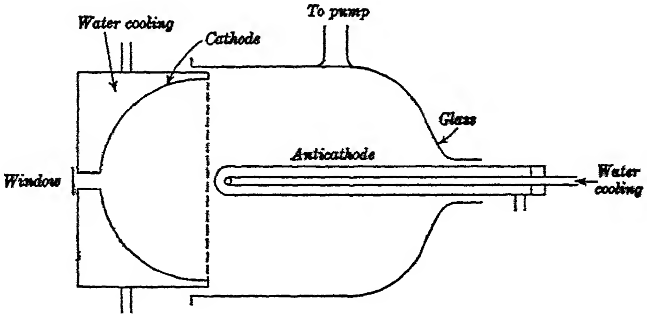

Fig. 103.

We may mention, finally, a new type of tube designed by W. Gerlach.[5] In this type of tube the cathode is a hemisphere of copper which simultaneously serves as one of the walls of the tube. The Roentgen rays, originating from a water-cooled anticathode placed centrally within the cathode hemisphere, emerge from the tube through a small opening in it which is closed by a window or filter of non-absorbing material (see Fig. 103). This tube may be modified in divers ways.

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[5] W. Gerlach, Verh. d. Deutsch. physik. Ges. 1921; also P. Cermak, "Roentgen Rays" (J. A. Barth, 1923).

Thus, C. Cermak utilizes a metallic tube and the anticathode filament is inserted along the axis of the tube, thus producing a thread-like source of X-rays.

A tube of this type may serve also as a "cathode ray furnace." The extremely intensive concentration of the cathode rays upon one spot of the anticathode will cause this metal to melt immediately.

H. Küstner[6] produces a linear radiation source by directing the cathode radiation almost tangentially to the surface of the anticathode. In this wise he obtains not only an increased intensity but also as pure a characteristic radiation as possible because the continuous spectrum has a minimum energy tangent to the anticathode.

To render Roentgen radiation monochromatic, filters of various types are employed: thus, an anticathode of copper with a filter of nickel will yield a spectrally pure K_α-radiation of copper, while a molybdenum anticathode together with a zirconium filter (0.05 gm. of ZrO_2 on collodion) produces the K_α-radiation of molybdenum.

Several improvements of real merit have also been attained in connection with the Debye-Scherer method. The definiteness of the interferences was increased to such extent by the use of slit-diaphragms[7] (instead of the ordinary opening) that the previously observed broad and hazy bands took on the appearance of sharp spectral lines. At the same time the intensity of the radiation to be reflected is increased many times. H. Küstner[8] accomplishes still more by using (together with his linear radiation source, previously mentioned) the substance under test in the form of thin wires or by applying it in the form of finely pulverized crystals as a very thin layer upon a silk thread. The silk thread can be drawn through the camera during exposure as a consequence of which (this is important in the case of the coarser powders) the crystal grains may be struck by the rays at divers angles.

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[6] H. Küstner, Physik. Zeitschr. 23, 527 (1922).

[7] W. Gerlach, Physik. Zeitschr. 22, 557 (1921); 23, 114 (1922).

[8] H. Küstner, loc. cit.

Strong absorbing powders may be "diluted" with the light organic substances (horn, cellulose).

Mention may be made at this point of two types of camera, due to O. Pauli[9] and H. Küstner,[10] respectively. The latter may be evacuated and is so constructed that it is impossible for reflected primary radiation, secondary or tertiary radiation from the metallic parts of the camera to strike the film. This is very important in the investigation of substances of low atomic weights and poor reflectivity, particularly of organic compounds and biological preparations.

Mix Crystals

L. Vegard investigated the structure of mix crystals by means of the X-ray method of Debye-Scherer. A comparative study was made of the photograms of KBr, KCl and mix crystals KBr-KCl obtained by monochromatic Roentgen radiation. The photograms of the latter show only single lines as do the photograms of the individual components, whereas mechanical mixtures of pulverized KCl and KBr give double-lines corresponding to the two components. The size of the elementary cube of the mix crystal is seemingly computable from the components by means of a simple addition law. If a_m, a_{KCl}, and a_{KBr} designate respectively the lengths of the cube of the mix crystal, and of the individual crystals KCl and KBr, we obtain

$$a_m = \frac{p - 100}{100} a_{KBr} + \frac{p}{100} a_{KCl},$$

where p is the molecular per cent of KCl in the mix crystal. The following a-values were[11] obtained,

	KBr	KCl	KBr-KCl
$a =$	6.597	6.290	6.442 Å.

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[9] O. Pauli, loc. cit. The evacuable form suggested by Pauli is not serviceable in this experiment.

[10] H. Küstner, loc. cit.

[11] For the preparation of mix crystals, see A. Fock, Zeitschr. f. Kristallographie 28, Vol. 4/5 (1897).

The reflection lines of mix crystals are sharply defined, the decrease in their intensity with increasing atomic number of the reflecting surface being equal to that of the pure components. It must be concluded, therefore, that the atoms mutually displace one another in the mix crystals, and that the replacing atoms all possess the same atomic diameter. This conclusion necessitates a variability of atomic volume, within certain limits. We may thus formulate a definition of mix crystal: mix crystals are bodies which are characterized by an irregular atom-substitution which is accompanied by a volume change of the atom (Vegard).

It is worthy of note that mixtures of KCl and KBr produced by mere mechanical trituration showed the lattice of a mix crystal; this indicates the formation of mix crystals by mere contact of the solid phases of the components (L. Vegard). This observation is more or less confirmative of Spring's viewpoint regarding chemical reactions in the solid phase. Copper-gold alloys were investigated by F. Kirchner. They all have a uniform lattice, a face-centered cubic lattice (NaCl-type). The validity of the additive law of Vegard's mix crystals is apparent here within fair approximations. In Figure 104, the line represents the lattice constants of the

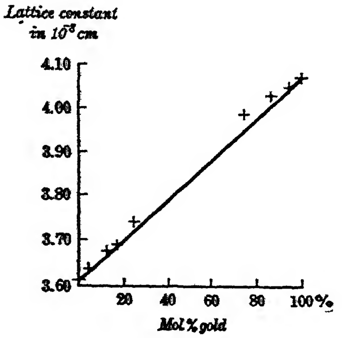

FIG. 104.

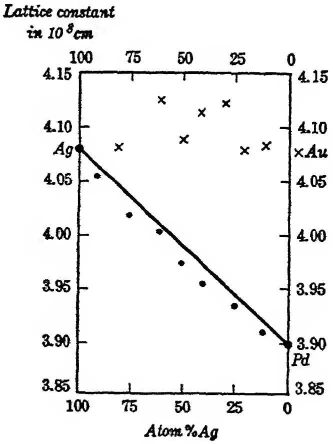

FIG. 105.

alloys as computed from the constants of copper and of gold on the assumption of the validity of the additive law; the experimentally measured constants are shown by the cross-marks. The agreement in observed and calculated values is obvious. Kirchner attributes the deviations from the additive law (too large values for the constants) to the influence of the greater atomic volume of the gold. McKeehan observed similar deviations in mixtures of palladium and silver (Fig. 105). This diagram shows likewise the results of an analysis of silver-gold mixtures (indicated by the cross-marks), both of which elements have nearly equal lattice constants: thus,

Silver	4.08 Å.
Gold	4.075 Å.

while the lattice constants for copper and palladium are respectively 3.61 and 3.90×10^{-8} cm.

We are entirely at a loss kinetically to account for the production of a uniform lattice by the substitution of atoms of one type by atoms of another type.

M. R. Andrews[12] investigated the same problem in his extensive researches on the structure of iron-nickel alloys, iron-cobalt alloys and copper-zinc alloys. He employed the powder method of X-ray analysis of Debye-Scherer[13] as modified by A. W. Hull.[14] The following changes in the crystal structure were noted as the per cent of the component elements varied. Thus, for iron-nickel alloys (percentages are given in terms of nickel), he found: from 0 (pure iron) to 25 per cent nickel, the resulting mix crystals possessed a space-centered lattice structure, from 25 per cent to 30 per cent, both space- and face-centered lattices adjacent to one another, from 30 per cent to 100 per cent (pure nickel) only face-centered lattices. Iron-cobalt alloys show a space-centered lattice from 0 per cent to 80 per cent cobalt; above 85 per cent cobalt only face-centered lattices appear, although cobalt itself is known both as space-centered and

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[12] M. R. Andrews, Physical Rev. 18, 245 (1921).

[13] Phys. Rev. 10, 661 (1917).

[14] Physik. Zeitschr. 17, 277 (1916); 18, 291 (1917).

as face-centered. Hexagonal lattices also seem to be present. Copper-zinc alloys are rather complicated, due, no doubt, to combination of the face-centered copper with hexagonal zinc. We may summarize the results of these copper-zinc mixtures as follows:

Per Cent Zinc	Lattice
0 = (copper)	Face-centered
0–47	Face-centered
47–50	Face-centered and space-centered contiguously
50–69	Space-centered only
69–79	Space-centered and rhombohedral
79–90	Rhombohedral only
90–100	Rhombohedral together with hexagonal
100 = (zinc)	Hexagonal

These results are in fine agreement with the results obtained from the thermal investigation of the zinc-copper system, as represented graphically in Tammann's metallography.

M. R. Andrews made the further observation that Fe + 25 per cent Ni, when in the magnetizable condition—it becomes magnetizable when cooled with liquid air—exists in the space-centered lattice form, while the non-magnetic alloys have a face-centered lattice.

K. Becker has shown by means of Roentgen analysis that the previously supposed compounds Ni_6W or Al_3Cu in reality are not compounds but mix crystals, probably indicating atomic substitutions.

Ferromagnetism and Crystal Structure

Iron-nickel alloys (25 per cent of Ni) were examined likewise by F. Kirchner. These alloys are of interest physically in many respects. They are magnetizable, but only if previously cooled by liquid air. The uncooled alloy or when heated to 580° C. is permanently non-magnetic ($\mu = 1.4$). A change in other properties also takes place.

	Specific Resistance	Tensile Strength	Specific Gravity
Magnetic condition	0.00052	135	7.98
Unmagnetic condition	0.00072	80	8.15

X-ray photographs show that the unmagnetic condition possesses a face-centered lattice and a well-defined lattice constant of 3.580 Å. (as calculated from the specific gravity, this is 3.576 Å., an agreement within 0.1 per cent). In the magnetic condition the space-centered crystal modification is prominent in addition to the face-centered lattice. This has a lattice constant of 2.826 Å. The lattice constant of space-centered modification, as calculated from the specific gravity, is 2.858 (spec. grav. 7.98) and 2.538 (spec. grav. 8.15), respectively; this is close agreement between experimental and calculated values. The difference between the magnetic and the non-magnetic mix crystals parallels a difference in their lattice structure. It is not evident, however, whether the difference in lattice is the cause of the differences in properties. In this connection it is very interesting to compare the findings of Wewer (in the Kaiser Wilhelm Institute for the study of iron). Wewer determined the lattice structure of α-iron (space-centered) and of γ-iron (austentite, face-centered). Austentite becomes strongly magnetic when cooled (magneto-elastic effect). Along with this, a portion of the non-magnetizable face-centered form is transposed into the magnetic space-centered variety without a change in the size of the grains. We do not know as yet whether the space-centered form of iron per se is intrinsically ferromagnetic; we do know, however, that it alone is magnetizable. It is apparent from this that the problem of ferromagnetism may be approached from this direction. Nickel crystallizes only as face-centered crystals; we cannot explain the phenomenon of ferromagnetism therefore by ascribing it to the space-centered lattice alone. A variation in the lattice structure by means of magnetism has never been observed.

Very exact lattice measurements have been carried out by Westgren[15] on pure electrolytic iron:

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[15] Zeitschr. f. anorgan. Chem. 98, 181; 102, 1 (1922).

Lattice Constant $a \times 10^{-8}$ Cm.

Temp. 15° (α)	800° (β)	1425° C. (δ)	space-centered
$a = 2.87$	2.90	2.93	
Temp. 1110° (γ)		1425° C. (γ)	face-centered
$a = 3.63$		3.68	

The dependence of the lattice constant upon temperature corresponds exactly to the thermal expansion. The δ-modification, therefore, is nothing else but α-iron; the presence of the γ-form of entirely different crystal structure in a limited temperature range, above and below that at which the α-modification exists, is very noteworthy. The influence on the lattice of the carbon absorption and of "ageing" has been a subject of frequent study.

Hydrogen Adsorption

Yamada and MacKeehan investigated the variations in the lattice of palladium produced by adsorbed hydrogen. The problem confronting investigation in this case is: does a compound form or is this merely an instance of solid solution? The latter alternative is true. The lattice of palladium increases progressively with increase in the amount of adsorbed hydrogen. For an adsorption of hydrogen 660 times the volume of the adsorbing palladium (corresponding to 29 per cent molar) the extension in the lattice was 2.8 per cent, whereas a mechanical extension of 2.9 per cent was measured. It was not possible to determine just where and how the hydrogen enters into the lattice because of the great difference in atomic numbers of palladium and hydrogen.

Electric Conductivity

Roentgen analysis may likewise aid in the solution of the problem of the electrical conductivity of metals—even though this may be of a negative character at first. We refer to the problems of "free electrons." It has been proposed by many observers that the free electrons, which are the principal factors in the electron theory of conductivity, may be considered as being "lattice electrons," so that a metallic crystal lattice may be conceived as being composed of metal-ions and of electrons. Such "lattice electrons" ought to be easily recognizable in the Debye-Scherer diagram of the light metals, e.g., of lithium, where the metal-ion has but two electrons. It has not been possible, however, to give evidence of these free electrons, notwithstanding the favorable proportion of 2 : 1, whereas in the case of salts, evidence of two electrons of one ion as opposed to eight electrons of the other ion was definitely established. Free electrons in the sense of "lattice electrons" do not exist.

Liquid Crystals

E. Hückel[16] and v. d. Lingen carried out a series of investigations to determine whether the so-called liquid crystals show a true lattice structure recognizable by means of X-rays. The results obtained are diametrically opposed to one another.

Hückel examined p-azoxyanisol, p-azoxyphenetol, dianisalazin in the solid, in the turbid and in the clear liquid condition as well as cholesteryl propionate in the three states, and he found no indication of interference lines suggestive of a lattice structure as soon as the various substances passed from the solid state into a "liquid" state, i.e., into a liquid state of turbid appearance in which state the substance is anisotropic.

F. Weigert[17] correlates Hückel's negative results with the phenomenon of double refraction which likewise is recognizable optically but not by means of the X-rays. We must conclude, therefore, that the optical anisotropy of "liquid crystals" may be attributed to the structural disposition of greater molecular complexes in which the individual molecules themselves are more or less inordered.

v. d. Lingen[18] fused p-azoxyanisol in thin films between

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[16] E. Hückel, Physik. Zeitschr. 22, 561 (1921). Discussion at the "Jenaer Physiker Tag."

[17] E. Hückel, Phys. Zeitschr. 22, 561 (1922).

[18] J. Stephen v. d. Lingen, Journal Franklin Institute 192, 511–514 (1921).

two mica plates and photographed the solidified melt according to Laue's method. Crystals of about 1 mm. extension were found in the melt. The space lattice structure remained intact also in the plastic state. Confirmation of these data is obviously necessary.

Of particular interest is the comparison of the infra-red absorption spectrum of the same substances in the solid, anisotropic liquid condition and in the amorphous liquid condition; no difference of any kind being observed in them.

Liquids

Very little is known regarding the "crystal state" of liquids. It is feasible to ascribe to them a microcrystalline condition. Proof of this has not yet been adduced, nor has full consideration been given to the fact that multiple reflection may simulate negative results.[19] Debye and Scherer[20] believed at first that they had established evidence of the structure of liquid benzol; somewhat later Debye[21] showed that his first explanation was incorrect and that the observed phenomenon was due rather to a general scattering of X-rays from irregularly placed molecules.

On the assumption that all molecules are equally spaced, W. H. Keesom[22] has shown the possibility of thus arriving at a practically useful calculation of such Debye-Scherer photographs of liquids. He examined oxygen, argon, benzol, water, ethyl alcohol, ethyl ether, and formic acid in the liquid state. From the radius of the deflection curves of the various substances he calculated the molecular distances. If this observed value $a_{\text{obs.}}$ be compared with the value computed from the density and the molecular weight according to the equation $1.33\sqrt[3]{M/d} = a_{\text{com.}}$, we will note a very good agreement in values. φ is the angle at which the interferences are evident.

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[19] W. Gerlach, Physik. Zeitschr. 22, 557 (1921).

[20] P. Debye and P. Scherer, Göttingen Nachrichten, 1916.

[21] P. Debye, Nauheim Lecture, 1920, unpublished, to the author's best information.

[22] W. H. Keesom, Physica 2, 118 (1922).

	φ	In Ångstrom Units	
		$a_{obs.}$	$a_{com.}$
Oxygen	27°	4.0	4.0
Argon	27	4.0	4.1
Benzol	18	6.05	5.9
Water	29	3.75	3.6
Ethyl alcohol	22	4.9	5.2
Ethyl ether	19	5.7	6.2
Formic acid	24	4.5	4.5

It is worthy of note that a second diffraction ring was observed in the case of water, oxygen, and argon; in the former instance this was weak, but more pronounced for the later substances; the corresponding angles were 46° (water), 46° (oxygen), 49° (argon). We may conclude from these that double molecules are present and calculate their respective distances to be 2.4, 2.4, and 2.3 Å. This polymerization, therefore, brings into the foreground the dipole character of water, the quadripolar (or octopolar) character of oxygen and of argon.

CHAPTER XXIV

THE PHYSICAL BASES OF PHOTOCHEMISTRY

It has been known for a long time that many chemical reactions are favored by electromagnetic radiations of certain wave-lengths and that chemical molecules are decomposed through the influence of such radiations, or made more complex by polymerization. Chemical interest centers especially upon these actions since the fundamental chemical processes of organic nature, the vegetable kingdom, are photochemical reactions. In our discussion of the physical bases of photochemistry, we do not propose to give an exposition of photochemical reactions, nor will we offer a physical explanation of their mechanism; this is not possible —with but very few exceptions—for there is no doubt that the intrinsic photochemical process, the primary reaction, differs entirely from that reaction whose course we follow from the results of the observed chemical change. This latter action is the result of, and follows upon, the true photochemical action, which causates these secondary chemical changes, the secondary reactions, which themselves are uninfluenced by the radiation. It is these primary actions that will be discussed in the following pages.

Absorption of energy by an atom or a molecule will transpose it into a physically different but more energetic condition, which is characterized also by a chemical reaction differing from that of the normal state. The absorbed radiant energy will be available to the atom especially in the form of potential energy which it can either transfer to other non-absorbing atoms or molecules or which may serve as the source of energy for chemical decompositions. Herein is contained that which we will designate as physical photochemistry.

A few words may first be said regarding the magnitude and the measure of radiation energy. With the introduction of the quantum theory into photochemistry, A. Einstein has exhibited not only the first experimentally comprehensible application of the quantum theory, but he has, in addition, founded scientific photochemistry by its means, and upon its basis he has applied the quantum theory to the most divers fields of natural science. This fact may well be emphasized at this time since attempts have been made in certain quarters within recent years to obscure and belittle his merits on the occasion of the awarding to him of the "Nobel Prize." As in the chapter on "photo-electric effects" and more generally in

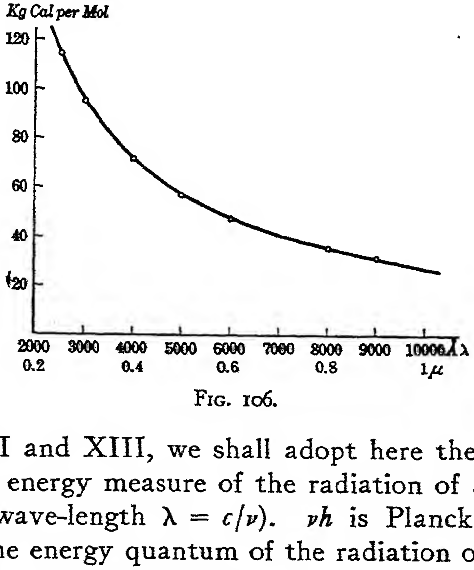

FIG. 106.

Chapters XI and XIII, we shall adopt here the magnitude $n \cdot h\nu$ as the energy measure of the radiation of a given frequency ν (wave-length $\lambda = c/\nu$). νh is Planck's radiation quantum, the energy quantum of the radiation of this given frequency ν. The effectiveness of a radiation is therefore proportional to its frequency. n is the number of these quanta in an energetically measured radiation $S = n \cdot h\nu$. For a direct comparison of this energy with chemical energies, it must be remembered that the magnitude "$h \cdot \nu$" refers to an atom, whereas chemical energies are usually expressed in terms of energy per gram-molecule. Figure 106 shows the relation of chemical energy per mole (ordinates), expressed in kilogram calories, and wave-length. This curve will be of service for many purposes. A radiation of wave-length 3,000 Å. = 3×10^{-5} cm. possesses an energy quantum

$$h\nu = \frac{6.55 \times 10^{-27} \times 3 \times 10^{10}}{3 \times 10^{-5}} = 6.55 \times 10^{-12} \text{ erg}$$
$$= 6.55 \times 10^{-12} \times 0.239 \times 10^{-7} = 1.565 \times 10^{-19} \text{ gr. cal.};$$

for a gram mole, this becomes $h\nu = 1.565 \times 10^{-19} \times 6.06 \times 10^{23}$ = 95,000 gr. cal. If, therefore, radiation of wave-length 3,000 Å. is absorbed, energy to the extent of 95,000 cal. per mol. will be available for subsequent chemical reaction.

As a fundamental requisite for the progress of a photochemical reaction, it is necessary that the "effective" radiation should also be absorbed. However, we must not conclude that a chemical reaction follows under all circumstances because of a previous absorption; it is possible that the absorbed energy, that is, the quantum $h\nu$, per atom, may be too small; or it may be also that the "excited" atom does not react with the other substances present at the same time. Modern physical research accomplishes an entirely new result: it reveals chemical actions which are entirely unknown in chemistry and which appear "impossible" from a chemical viewpoint. One such example is the reactivity of helium while in a more energetic, excited state. The radiation absorbed by the helium atom is of exceedingly short wave-length; in fact, the wave-length is so short that it is inaccessible at present for laboratory measurements. But it is known that electronic impact will elevate an atom into the same energy state (energy level) into which it is brought by the absorption of the first line of its principal series. This excited helium atom is a "quasi" alkali atom: one of its electrons is distantly removed from the atom, i.e., it has one "valence electron." In order to transform the helium atom into this alkali-like state, nearly 500,000 cal. are required per mole, an exceedingly large energy from the chemical point of view. Chemical compounds of helium are not known; this is due to the fact that excited helium atoms of this type are altered to such an extent—by the mere presence of other atoms—that they revert immediately into the normal condition of the noble gases with attending evolution of energy. On the other hand, the formation of helium molecules of at least momentary stability is demonstrated by the spectroscopic examination of helium stimulated to incandescence. We know that atoms emit line spectra, while molecules on the other hand are characterized by band spectra. Such band spectra are emitted by helium, e.g., when stimulated electrically in Geisler tubes. These band spectra unmistakably establish the existence of helium compounds whose analysis shows them to be heteropolar He_2 compounds. The "excited" helium atom in this quasi-alkali condition is more electropositive than is the normal helium atom, both combining to form a molecule. The spectra of all monatomic gases and vapors show such bands, indicating that they are partly combined to produce double molecules; the number of the various double molecules becomes larger if a portion of the atoms is previously transposed into higher energy levels. Since such higher energy levels may likewise be brought about by the action of light, their formation represents the simplest type of photochemical reaction.

More will be said, in detail, in the following chapters regarding similar instances. They are differentiated from one another in one respect; the energy absorbed by a given atom, i.e., the excess energy of the "excited state," is consumed in bringing about a change within an atom or molecule which may collide while in the normal condition with an "excited" atom. The reaction discussed more fully below is of this type: we refer to the longest known photochemical reaction which has been explained satisfactorily only very recently, viz.: the photochemical formation of HCl from its constituents hydrogen H_2 and chlorine Cl_2. This reaction always proved notable because in it—as was the usual formulation—light merely played the rôle of a catalyst; a small amount of radiation capable of being absorbed by chlorine sufficed to cause large quantities of chlorine Cl_2 and of hydrogen H_2 to enter into chemical combination; an appropriate stimulus

(Anstoss) was the only thing necessary and the reaction subsequently proceeded of its own accord. Nernst first attempted to explain this reaction by means of "chain-reactions." Through the influence of light, chlorine atoms are first formed from chlorine molecules, i.e., the chlorine dissociates; the free chlorine atoms will then react as follows:

$$Cl + H_2 = HCl + H$$

$$H + Cl_2 = HCl + Cl$$

$$Cl + H_2 = HCl + H$$

etc.

(This series of chain reactions will continue until the process is "run out" because of the presence of impurities or because of the direct combination of the free atoms of hydrogen and chlorine to H_2, Cl_2 or HCl.)

Many difficulties confront this explanation. A. Coehn has demonstrated rather recently that the reaction will not take place at all when subjected to blue-violet radiation provided all traces of water vapor have been removed, even though chlorine itself absorbs this radiation. On the other hand, in the presence of water vapor the reaction progresses very rapidly. To explain this we will make use of Stern and Vollmer's interpretation of the elementary photochemical process. It is quite certain that chlorine Cl_2 molecules are not dissociated (as postulated above) by the action of absorbed radiation but are converted into an "excited," a more energized state. This "active" state may now be conceived as reacting in a manner as shown experimentally by Franck (for detail see Chap. XXV): an atom or a molecule in the active state may transfer its excess energy during collision to the "struck" atom or molecule if the latter is capable of utilizing it, i.e., if the energy is large enough to change the recipient atom or molecule. Now, the smallest energy amount that is absorbable by a hydrogen molecule is that which can dissociate it into its two atoms. The energy necessary for this is, however, far in excess of that energy quantum which the chlorine molecule Cl_2 may receive as the result of the absorption of either blue or violet light. The active chlorine Cl_2 molecule (which we may designate as $(Cl_2)'$) will thus not be able to change the hydrogen H_2 molecule; it may, however, transfer its energy to another chlorine molecule and thus produce chlorine atoms,

$$(Cl_2)' + Cl_2 = Cl_2 + 2Cl,$$

which, in connection with water, will give rise to the "chain reactions":

$$\begin{gathered} Cl + H_2O \rightarrow HCl + OH \\ OH + H_2 \rightarrow H_2O + H \\ H + Cl_2 \rightarrow HCl + Cl \\ \text{etc.} \end{gathered}$$

Later experiments by Coehn seem to confirm such a series of actions; if chlorine absorbs a much larger quantum $h\nu$, e.g., if it absorbs ultra-violet light (larger ν), the reaction will proceed even if thoroughly dry; the energy of the exciting state $(Cl_2)''$ will now suffice to dissociate the hydrogen molecule; the primary reaction will thus be

$$(Cl_2)'' + H_2 \rightarrow Cl_2 + H + H,$$

from which we will have

$$2H + 2Cl_2 \rightarrow HCl + Cl_2$$

without any "chain reactions" whatever.

Thus far, however, we have considered only the qualitative side of Einstein's conception. Einstein's law is, however, a quantitative formulation according to which each absorbed quantum $h\nu$ should give rise to an elementary photochemical action. In the HCl reaction mentioned above the secondary action follows so rapidly upon the primary action that it was not possible hitherto to give proof of the individual actions. For a number of years E. Warburg quantitatively studied simple photochemical gas reactions; his data establish the validity and applicability of Einstein's "law of the photochemical equivalent" for photochemical reactions in which the secondary action is definitely determinable. In other words, if radiation to the extent of $S = nh\nu$ is absorbed, the number of "absorbing" molecules as well as the number of "reacting" molecules are both equal to n. Each molecule, therefore, absorbs a quantum $h\nu$ and each "activated" molecule is chemically reactive.[1] Other determinations of gaseous and also liquid reactions, recently carried out by Nernst and coworkers, substantiate and confirm this law.

Eggert and Noddack investigated a very important photochemical problem: the applicability of Einstein's "equivalent law" to the photochemical actions arising on a photographic dry plate.[2] The significance and importance of their results lie not only in the explanation of this technically important photochemical action, but also in testing the validity of the law of equivalents as applied to solid bodies.

The photochemical action consists in the disruption of a silver bromide molecule by the absorbed radiation into an atom of silver and an atom of bromine. On Einstein's law of equivalents, a definite quantum $h\nu$ is requisite and sufficient for each and every action of this type. The quantity of silver, that is, the number of silver atoms, separated in this manner through the action of a measured amount of radiation is determined in the undeveloped plate by chemical means. Assume N quanta of radiation are incident upon the plate and let the number of measured silver atoms be designated by A; then $N = A$, provided each of the N quanta becomes effective. But such is not the case. A portion of the incident radiation is dissipitated by reflection from the plate; another portion gets lost because of the partial transparency of the plate as a result of which not all the incident light is absorbed. The ratio

$$\frac{\text{Number of silver atoms}}{\text{Number of incident quanta}} \quad \frac{A}{N}$$

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[1] For details, the reader is referred to W. Gerlach, "Foundations of the Quantum Theory."

[2] J. Eggert and W. Noddack, Berl. Ber. 1921, 631.

consequently cannot be equal to 1, but it must be equal to the absorption power of the dry plate if Einstein's law is valid. The absorption power was carefully determined for several plates and the following data obtained:

Type of Plate	A/N in Per Cent	Absorption Power in Per Cent
Agfa-Reproduction	3.2	5
" "	3.2	8
Agfa-Roentgen	1.95	4
Agfa-Special	10.8	11.4

(a sufficient and fair enough agreement in view of the difficult character of the experiment). We may therefore consider the law of equivalents as valid and applicable to photochemical reactions in solid bodies.

Objections have been raised against these conclusions by F. Weigert, objections that seem substantiated by experiment. It is obvious, therefore, that we must await further experimentation in order satisfactorily to explain these results.

The work of P. P. Koch (and coworkers) on the photochemical actions taking place on microscopic and ultramicroscopic silver bromide crystals is of great interest. The granules were isolated and individually subjected to experimentation. By the results of many other investigations (Vogel, Schaum, Volmer, et al.) it can scarcely be doubted that the process of light sensitization of silver bromide takes place between the initial condition $(Br^- Ag^+)_n$ in the crystal lattice and the final condition $(Br^- Ag^+)_m$ in the crystal lattice + (Ag) + (Br_2). The more recent experiments, already cited, utilized the method which Millikan and Ehrenhaft employed in their investigations on the existence of an elementary electrical quantum. Free granules of silver bromide—recognized as crystal fragments of AgBr by Roentgenographic investigative methods—were introduced between the horizontal metallic plates of an electrostatic condenser. The gravitational motion of such small grains, whose masses are of the order 10^{-11} grams, may be neutralized by establishing an electric field between the plates; since such small particles invariably are charged electrically (or may become charged very easily by a momentary subjection to radium illumination), the imposed electric field E may so be measured and adjusted that the force eE operative upon the electric charge e of the crystal particle is equal to and neutralized by the gravitational force mg effective upon the particle. If the particle's mass is m, we have

$$eE = mg.$$

For details of this method we refer the reader back to Chapter VI. However, there is this difference. Whereas the condenser method served then (in Chap. VI) as a most sensitive electrometer—to detect a variation in the charge of the elementary quantum, the electron—it is utilized primarily in these experiments as a micro-balance. As is apparent from the above equation, the balance is disturbed by variations in mass as well as changes in charge (see p. 124).

Such particles were illuminated, accordingly, with very intensive radiation and gave evidence of a decided decrease in their mass which after a while becomes constant;[3] the mass variation oscillated for different particles within rather wide limits, but they were always detected. Silver chloride showed the same effect, but not so silver iodide, and likewise blank tests with barium sulphate, copper or dust particles.

The procedure was very clear for different—weaker—illumination: proportionate to the weakened light energy the time interval (to bring about a given photochemical effect) becomes greater, the increase being of such order as to indicate an approximate concordance with the Bunsen-Roscoe law (intensity × time = constant, produces equal photochemical effect).

On the other hand, for still more pronounced decreases in the light intensity, equal light quantities (It) produce a considerably larger bromine yield for stronger intensities operative during a small time interval than do smaller

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[3] P. P. Koch and B. Kreiss, Zeitschr. f. Phys. 32, 384 (1925).

intensities during a correspondingly larger period of illumination. Obviously, there is question here of a recombination effect of the primarily decomposed molecules.

Furthermore, it has been determined that bromine escapes as a neutral gas, that no changes in charge arise with variations in mass (as may be shown from the motion of the mass and application of Stokes' law; for theory, see Chapter VI); moreover, we can show also that the exterior form of the particles is essentially changed after the release of the bromine.

Perhaps these observations will make possible the eventual explanation of the elementary reactions whereby the formation of free bromine takes place.

CHAPTER XXV

Luminescence in Chemical Reactions

We have become familiar with the following methods of the photo-excitation of atomic rays: thermal excitation, electronic impact and excitation by means of radiation. The simplest method of excitation of the emission spectrum, the introduction of the substance in a finely divided state into a gas flame by means of a blast, seems to contain another, unknown, effect. This conclusion is evident from the following considerations: when sodium vapor is introduced, together with air, into a blast flame, the inner cone of the flame will be more luminous in the yellow light (D-lines) than the outer cone, even though the measured temperature of the former is lower (about 1,500–1,600°) than the latter (about 1,800°). The question arises therefore: may this difference in stimulation be attributed to a more efficient utilization of the energy by the one flame, or is an additional energy of a chemical nature operative? It is not possible to answer this question by means of an experimental arrangement analogous to the blast flame, due to the large number of gaseous reactions involved. Furthermore, both the mechanism of the chemical action as well as the nature of the observed emission must be known, if an explanation of the emission process is sought in the combination of both these factors. F. Haber and W. Zisch[1] observed that sodium vapor in an halogen atmosphere (e.g., chlorine) yields a yellow flame with the simultaneous formation of sodium chloride (NaCl) and that this flame can be maintained at so low a temperature[2]

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[1] F. Haber and W. Zisch, Zeitschr. f. Phys. 9, 302 (1922).

[2] This flame may be produced as follows: a current of nitrogen is led over sodium in a heated glass tube; becomes saturated with sodium vapor and enters, as such, through a passage of several millimeters in a second heated glass tube, into which a current of dry chlorine gas of same temperature is passing. The temperature always remained below 500° C.

that an emission visible to the eye is not explainable on the basis of thermal excitation alone. It appeared reasonable, therefore, to attribute the excitation of sodium lines—proved present in the yellow illumination by means of the spectroscope—to the chemical energy of formation of the sodium chloride molecule.

It is not compatible, however, with our accepted views in the emission of line series to assume that the radiation of the sodium atom be emitted by the sodium chloride molecule. A line-series emission is peculiar to the free atom and is radiated during the passage of the valence electron from orbits of higher energy to orbits of lower energy (a process opposite to a chemical reaction), the radiated energy $h\nu$ being equal to the energy difference ΔE of these two orbits or atomic states. Furthermore, the intensity of the D-line emitted by the sodium chloride flame is much too weak in comparison to the number of sodium chloride molecules formed to attribute the emission to them. And finally, it is not known that very energetic chemical reactions emit a more intensive radiation than corresponds to the thermal radiation. If, therefore, the emission of the D-line is due in some way to a chemical reaction, it is necessary that the energy of the reaction be transferred by means of some mechanism from the reaction product to a sodium atom not participating in the reaction.

When a molecule AB is formed from two gaseous elements A and B, there first will be formed, as a primary reaction product, an "energized" molecule, i.e., a preliminary transitory molecular product of unknown mode of combination; this activated molecule contains within its structure the total available reaction energy. We will designate this by $(AB)'$. So long as this "reaction heat" is not removed from this intermediate molecule, the formation of the eventual molecule AB does not take place completely. The intervention of another atom is thus necessary to withdraw the excess energy from the activated molecule; furthermore, this third atom must intervene immediately upon the formation of the intermediate molecule $(AB)'$ inasmuch as this may again decompose ("triple collision" is requisite for molecule formation). The withdrawal of the excess energy can be accomplished by its conversion into kinetic energy of the third atom. However there is still another possibility. If such an activated molecule collides with an atom A, which can be transformed by the available excess energy of the molecule, it may transfer its energy to atom A without its previous conversion into kinetic energy, thereby elevating A to a state of higher energy content A'. The number of such A'-states is not variable and indefinite, but is a fixed quantity depending upon certain quantum conditions; these A'-atoms, thereupon, may revert into the normal atoms with the simultaneous emission of their excess energy in the form of a monochromatic radiation. These several actions may be formulated as:

$$A + B = (AB)'$$
$$(AB)' + A = AB + (A)'$$
$$(A)' = A + h\nu.$$

In other words, the "chemical" energy has been emitted. For this transformation to take place it becomes requisite, therefore, that the available chemical energy associated with the molecule $(AB)'$ be equal, at least, to the energy necessary for the excitation of the lowest excitation state of the atom. This condition obtains in the case of the formation of sodium chloride molecules from gaseous sodium atoms (A) and chlorine atoms, $\frac{1}{2}Cl_2$, (B). The difference of the energy of a mole of sodium chloride vapor as opposed to the energy of a mole each of sodium vapor and chlorine gas is 77 cal., whereas the energy calculated on the quantum theory for the excitation of the D-line ($\lambda = 5{,}893$ Å.) is only 49 cal. per mole, as computed from the expression $E = JNh\nu$ (wherein N is Loschmidt's number, 6.06×10^{23}, and J the conversion factor ergs-cal.). The energy of the chemical reaction thus suffices for the excitation of the D-line.

Conditions are somewhat different in the case of mercury.

If this is substituted for the sodium in the previous case, a flame results together with the simultaneous formation of mercury chloride ($HgCl_2$) and a green-blue band emission. The heat developed during the formation of mercuric chloride ($Hg + Cl_2 = HgCl_2$) is only 53 cal., whereas the energy needed for the emission of the first line of the mercury spectrum, i.e., the energy requisite to produce the first excitation state of the atom, is 111 cal. ($\lambda = 2{,}537$ Å.). No trace of this line was observed in the emission spectrum of the flame. Statements of a quantitative character cannot be made at this time regarding the excitation of the observed band spectrum.

There is thus demonstrated a new type of energy transfer from a molecule of high energy content to a normal atom by converting the latter into a higher quantum state.

This conception of Haber and Zisch is confirmed by the observations of J. Franck[3] and the relevant experiments of Franck and Cario. Klein and Rosseland for some time had drawn attention to the following: in a mixture of atoms and electrons the latter are accelerated by electric fields; they are then empowered to transfer their kinetic energy of translation to atoms provided this be large enough to transpose the affected atom into one of its possible higher energy states. This is identical with the previously discussed quantum excitation of atoms. When such an activated atom collides, during its life period, with an electron at rest, it will transfer its excitation energy, in turn, to the electron in such a manner that it will reappear as kinetic energy of the electron. This theory of Klein and Rosseland is not readily susceptible of proof in this form because of experimental reasons.

Nevertheless, verification of this viewpoint seems possible if we recall that molecular collisions of sufficient kinetic energy can also occasion quantum transformations, as indicated by thermal emissions, provided the relative kinetic energy E of two colliding atoms is equal to, or larger than, the excitation energy $h\nu$ of the frequency ν of one of the atoms,

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[3] J. Franck, Zeitschr. f. Phys. 9, 259 (1922).

as determined on quantum principles. The question thus arises: can a collision of an activated atom with an unactivated atom bring about a direct transfer of energy from one atom to the other, in a manner other than by a transition from kinetic energy into potential energy. Evidence of such excitation would be, on the one hand, the complete analog to "Klein-Rosseland" impact of the second type and also would be perfectly analogous to the process that must be assumed for the interpretation of Haber-Zisch experiments.

The experimental procedure is somewhat as follows: a mixture of two metallic vapors, *A* and *B*, is illuminated with monochromatic radiation of such wave-length that it is absorbable by one of the atoms, but not by the other. The energy of this absorbed frequency ν must be greater than the requisite excitation energy of the second atom. If activated atoms $(A)'$ collide with unexcited *B*-atoms, and a transfer of the energy previously absorbed by *A* (to produce $(A)'$) takes place at the same time, we may anticipate the production of $(B)'$-atoms, and upon the reversion of these activated forms to the normal *B*-atom, we may expect the emission of the spectral lines peculiar to this atom. A mixture of mercury vapor and thallium vapor is illuminated with the mercury resonance (or absorption) line $\lambda = 2{,}536.7$ Å. This wave-length is absorbed only by the mercury atom and not by the thallium atom. The activated mercury atom, (Hg)′-atom, re-emits this absorbed radiation in part as resonance radiation, and in part also transfers it to thallium atoms during collisions of the (Hg)′-atoms with thallium atoms, Tl-atoms, transposing the latter into an activated state (Tl)′; there results a simultaneous emission of the thallium lines, whose excitation energy is smaller than the energy available, $h\nu_{\text{Hg}\,2.537}$. Upon the addition of silver vapor, the silver-lines also appear in the emission. The experimental procedure is shown in Fig. 107.

The evacuated quartz vessel 1 contains thallium, and vessel 2 mercury; both vessels are heated electrically to a vapor pressure of a few millimeters; in vessel 1, therefore,

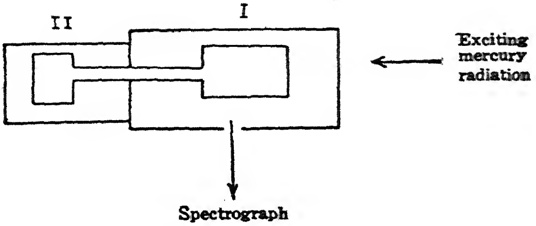

FIG. 107.

there will be present a mixture of mercury and thallium vapors (in other experiments silver, sodium, bismuth, lead, etc., were substituted for the thallium). Mercury radiation from a mercury-in-quartz-lamp is projected into vessel I; of this radiation the line λ = 2,536.7 alone will be absorbed. Thallium lines appear very prominently in the emission which was measured perpendicular to the direction of the exciting radiation. The upper exposure of the following photograph shows this effect; the thallium lines are indicated by their respective wave-lengths. The fact that mercury lines also appear is of secondary importance; they are due to the radiation of the mercury lamp reflected from the walls of vessel I. The second exposure (lower) shows this radiation alone, obtained when the mercury only was vaporized.

We shall study the significance of these results in a later section (see Chapter XXVIII).

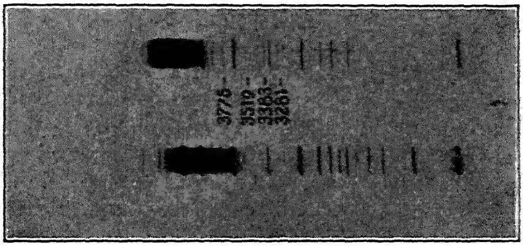

FIG. 108.

The quantum transfer of the excitation energy absorbed by an atom, or of the energy of formation disengaged during the production of a molecule from its constituent atoms and still present in the molecule, to a normal atom with a concurrent transformation of the latter into an activated state—provided the energy available is sufficient thereto—is thus definitely established. Should the primary excitation energy prove too small and thus not be capable of accomplishing the conversion of the normal atom into an activated state, the energy disengagement obviously will not take place in a single action, in the case of $HgCl_2$ studied by Haber and Zisch. It is not known just what action does take place in these cases. It is very expedient, however, to conceive that the energy is present in the above named primary product $(AB)'$ as radiable "Austrahlbar" energy. This can be emitted and the resulting emission must be a band spectrum; this much is indicated by the spectrum emitted during the conversion of mercury to mercuric chloride.

Without forming any definite notion of the nature of the more energetic $(AB)'$-product, or of the manner in which it retains the energy or releases it—that is, on the basis of the formulation employed thus far, that the primary reaction product contains the energy of formation as potential energy—we may consider still another class of phenomena along similar lines: ionization by means of positive ions. A positive ion may be viewed in a certain sense as an energized reaction product whose components are, respectively, the ion and a distantly removed electron. During their recombination energy will be released. If now a positive ion of an element *A* with a high ionizing energy collides with an atom *C* of lower ionization potential, the former will exert a stronger electron affinity for an electron *B* of atom *C* than will be exerted by the ion of *C*. We may, accordingly, regard the ion *A* and an electron of atom *C* (as *B*-constituent) as the primary product $(AB)'$; the ionization of atom *C* may therefore be considered as the first step in the disengagement of energy during the gradual recombination of ions of *A* to neutral atoms. If the ionization potential of *A* is considerably larger than that of *C*, still more energy will be liberated until the final neutral form of atoms *A* has been attained; this additional energy will become apparent in the ionization of more *C*-atoms. This would be the "ionizing capacity" of the positive ions. There is still another possibility. A positive ion of *A* may combine with a neutral atom *C* to form a compound of greater energy content $(AC)'$, which, in turn, may so release its energy as to ionize other *C*-atoms. If the disengagement of energy takes place in the form of a radiation, it will doubtlessly be observed as a band spectrum; it must, furthermore, be a short wave radiation since this is effective in ionization. The experiments of Polany, Beutler, Kallmann, Fränz, Lialikow, Terenin, et al., show how much we are still in the dark as regards this problem. The disengagement of energy according to Haber would indicate a monochromatic radiation of another atom of sufficiently smaller excitation energy, in addition to the $(AB)'$ atom. The excitation energy necessary can only be a monochromatic radiation of the same frequency as the excited radiation; for as far as we now know, a spectral line is excited during excitation by radiation (resonance) only by an exactly equal frequency. The principal line (D-line of sodium) of the spectrum can be excited by other frequencies only if these first ionize the atom; during recombination, however, the entire line spectrum of the sodium atom will be emitted in addition to the D-line. It is evident, therefore, that it is of paramount importance further to investigate the process of ionization by positive ions as well as Haber's "flame-illumination"; thus, it would be of interest to know whether band spectra arise in both phenomena, whether monochromatic line-series are present during ionization by ions, and finally whether the principal series only arises during the "Haber-Zisch radiation" and whether ionization takes place also.

The possibility of a direct transfer of the chemical reaction energy of a $(AB)'$ molecule to an atom or a molecule not participating in the reaction is demonstrated by the work of Kautsky and Zocher,[4] in which is described a band

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[4] E. Kautsky and Zocher, Zeitschr. f. Phys. 9, 267 (1922).

chemiluminescence emitted in a reaction of silicon hydroxide, in all probability by non-reacting molecules. (Other examples are also given.) Chemiluminescence doubtlessly plays an important part in "flame illumination," even though this phenomenon is conditioned primarily upon thermal factors.

CHAPTER XXVI

ELECTRON-AFFINITY

A further application of the quantum theoretical considerations is had in the calculation of electron affinities. We shall discuss this topic in detail, since it lends itself readily to quantum theoretical explanations. By electron-affinity of an electro-negative atom, we understand the energy liberated when such an atom combines with a free electron to produce a negative atom-ion. That an "electro-negative" atom should possess such an electron-affinity—whence its name—is evident, among other things, from the familiar fact that such an atom is present in heteropolar compounds as a negative ion; furthermore, it migrates as the negative ion during electrolysis, and, finally, the concentration of free electrons is very small in halogen flames.

We may ask, therefore: what happens to the energy thus set free? Energy is consumed during ionization, i.e., in cleaving an electron from an atom, the atomic residue being positively charged (positive ion). The reciprocal process, the recombination of such a positive ion with a free electron, is analogous energetically to the previously described formation of a negative ion, i.e., it takes place with a concomitant disengagement of energy. The problem of what happens to the energy released during recombination of a positive ion with an electron has been solved: the liberated energy is transformed as is known into radiation; if the recombination takes place undisturbedly in an elementary process, the energy will be emitted, according to the quantum law (frequency-relationship), as a monochromatic radiation of frequency ν, whose value may be calculated from the ionization energy $E_J = h\nu$, or $\nu = E_J/h$, wherein h is Planck's universal constant. The frequency emitted constitutes the limiting frequency (head) of the optical spectrum of the normal atom. The correctness of these relationships has been definitely determined by experiment.

The same considerations may be applied to the transition of the neutral atom into a negative ion; i.e., we may conceive the energy liberated when an electron combines with a neutral atom, to be emitted as radiant energy; we may, accordingly, devise experiments to detect such emissions. J. Franck[1] has accomplished this on the following consideration. Let E_E denote the electron-affinity; in accordance with the above statements, a frequency ν should be emitted, so that $\nu = E_E/h$. It has been assumed, however, that the energy of the free electron prior to its combination with the neutral atom is zero, in other words, the electron was assumed to be at rest. Generally, this is not the case, since the electron possesses more or less kinetic energy—due, in part, to its thermal motion and partly because of the motion imparted to it by the electrical force of the discharge—which likewise must be liberated during the formation of the negative ion. In calculating the frequency ν of the emitted radiation according to the equation mentioned above, due attention must be paid accordingly to the liberation of the electron's kinetic energy as well as to the electron-affinity; there will thus appear, in place of the single frequency ν, a continuous spectrum of frequencies

$$\nu = \frac{E_E}{h}, \quad \frac{E_E + (\frac{1}{2}mv^2)_1}{h}, \quad \frac{E_E + (\frac{1}{2}mv^2)_2}{h}, \quad \ldots,$$

respectively, wherein the kinetic energy may possess any assignable value—at least probably so—from zero up. A continuous spectrum displaced sharply toward the red end may therefore be anticipated; the red end of the spectrum, the longest wave of this continuous spectrum, corresponds to the smallest ν, i.e., to the electron-affinity itself, since the second term of the sum in the numeration of the expression $\frac{E_E + \frac{1}{2}mv^2}{h}$ becomes equal to zero in the boundary of the

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[1] J. Franck, Zeitschr. f. Phys. 5, 428 (1921).

spectrum. Furthermore, the spectrum must be bounded also in the short waves; this will take place if the kinetic energy of the electron will be large enough to activate the atom upon impact.

This emission, anticipated on the basis of Franck's theory, is designated briefly as "electron-affinity spectrum."

It seems altogether probable that Franck's conception of the optical measurement of electron-affinity is correct. However, two points of the theory still need discussion. In the first place, it is known from experiments of Franck that iodine molecules, I_2, are characterized by a definite electron-affinity and consequently there should be a spectrum corresponding to the operation of this electron-affinity. In the second place, precisely the comparison—alluded to above—with the recombination radiation requires that the well-known possible appearance of all the lines of the spectrum in addition to the limiting frequency be explained; in other words, the possibility of intermediate stages between the ionized state and the normal state, while the formation of the negative ion is said to proceed without any possible intermediate states. J. Franck has offered the answer that the combined electrons in ionic formation move in the electrical field of a neutral atom whose strength becomes perceptible only in close proximity to the atom. If intermediate stages are present, therefore, it is possible to assume that these stages differ very little in energy.

It would be of interest to procure experimental data on this problem. This is especially significant since the investigations carried out to date on the spectra of the halogens in emission, absorption and fluorescence emissions do not give evidence of the existence of this "electron-affinity spectrum." Experimentation along the lines undertaken by Angerer and Müller (upon a suggestion of K. H. Herzfeld) appears most promising in this connection. It is known that vaporous salts dissociate at elevated temperatures partly into atoms and partly into ions; that is, negative atom-ions of the halogens are present in such vapors. If Franck's theory is correct, that is, if the energy of the electron-affinity is emitted as radiation during the formation of the ion, the reciprocal action should likewise take place; in other words, this radiation should be absorbed by the ion with the simultaneous cleavage of the electron. As a fact, Angerer and Müller observed absorption spectra in the vapors of halogen salts. It cannot be claimed, however, that this was the electron-affinity spectrum, even though the approximate concordance of these optically determined E_E values with the theoretically anticipated electron-affinities does not contradict the correctness of this explanation.

Electron-Affinity of	Absorption Wave-Lengths	E_E[2]
Fluorine determined by abs. in KF	3,030 Å.	94.0 cal.
Chlorine " " " " NaCl	3,280 "	86.6 "
" " " " CsCl	3,170 "	89.6 "
Bromine " " " " KBr	3,590 "	79.1 "
" " " " CsBr	3,490 "	81.3 "
Iodine " " " " KI	3,980 "	71.3 "

A few more words on the method of calculating electron-affinities according to Born.

This method is based upon the consideration of the energies involved in the formation of a salt from its constituents, e.g., the formation of potassium iodide from potassium atoms and iodine atoms. Assume a "solid" potassium atom $\overline{\mathrm{K}}$ and an iodine atom in gaseous molecular iodine $\frac{1}{2}\mathrm{I}_2$. These reactants will combine, with a disengagement of heat of formation Q, to produce the solid salt molecule $(\overline{\mathrm{KI}})$

$$\begin{tikzcd}
 & \overline{\mathrm{K}},\ \overline{\tfrac{1}{2}\mathrm{I}_2} \arrow[dr, "+Q"] & \\
\mathrm{K},\ \mathrm{I} \arrow[ur, "S", "D"'] & & (\overline{\mathrm{KI}}) \arrow[dl, "-U"] \\
 & \mathrm{K}^+\ \ \mathrm{I}^- \arrow[ul, "-E"', "+I"] &
\end{tikzcd}$$

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[2] Given as calories per mole.

In order to obtain from the salt molecule its constituent atoms in their initial form, it will be necessary first to separate the molecule into its ions, thereby producing the gaseous ions K^+ and I^-, whose formation involves the absorption of the so-called "lattice-energy" U. The potassium ion, thus formed, must now be transposed to the normal atomic state by the assumption of an electron, during which process the ionization energy I is liberated; at the same time the electron-affinity E will be absorbed to neutralize the negative iodine atom by cleaving an electron from it. There now remains the final step of transforming the gaseous potassium into solid potassium and the simultaneous conversion of the halogen atoms into molecular gas; this last stage takes place with disengagement respectively of the heat of sublimation S of the metal and the heat of dissociation D of the halogen molecule. We thus have a cyclic process in which the summation of the energies of the individual stages must equal zero. All the energies involved in this cycle are known with the exception of the lattice energy U and the electron-affinity E. The former may be calculated on Born's theory and, in conjunction with the other known values, gives E. The values are:

	According to Born	According to Angerer-Müller
E_{chlorine}	86 cal.	88
E_{bromine}	86 "	80
E_{iodine}	79 "	71

It would be much better, however, to determine the electron-affinity experimentally and then to calculate the lattice energy U by means of Born's Cycle in order to test the theory of lattice energy.

CHAPTER XXVII

CHEMICAL REACTIONS BY MEANS OF ELECTRONIC IMPACT

It has been known for decades that a considerable number of gaseous reactions take place under the influence of an electric discharge; such reactions are usually termed "silent discharge reactions." A technical example of such a reaction is the ozonizing of atmospheric oxygen in the purification of water on a large scale. There is no doubt that the chemical reactivity exhibited by certain gases under the influence of the electric discharge is due to the excitation experienced by the gas while in the path of the discharge, the dissociation or the ionization of one or more reacting substances. The nature of these reactants, however, has been unknown for practically all reactions.

The elaboration of the electronic impact method for photo-excitation has provided a new quantitative method for examining chemical reactions induced by electronic impacts. Such an investigation was undertaken recently by E. Buch-Andersen.[1] The formation of ammonia from hydrogen and nitrogen was selected as a typical reaction; the primary object of the investigation was "the determination of the minimal electron energy requisite for the formation of ammonia." It seemed probable from the beginning that the nitrogen is activated by the electric discharge, inasmuch as the reactivity of "nascent" nitrogen is known, whereas nascent hydrogen does not react with nitrogen. Consequently if it is atomic nitrogen that combines with the hydrogen to form ammonia, it may be anticipated that an electron energy corresponding to the dissociation work of the nitrogen molecule would suffice to induce this reactivity. Opposed to this, however, is the definitely proved experimental fact that nitrogen (as in the case of hydrogen described above) does not take up this

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[1] E. Buch-Andersen, Zeitschr. f. Physik 10, 54 (1922).

electron energy of approximately 4 volts,[2] just as it does not absorb the corresponding radiation quantum—wave-lengths between 3,000 and 2,000 Å. to which region it is thoroughly transparent. It seemed feasible, therefore, directly to determine the minimum energy requisite for NH_3-formation, if only to obtain further data regarding the influence of electronic energy upon polyatomic gases.

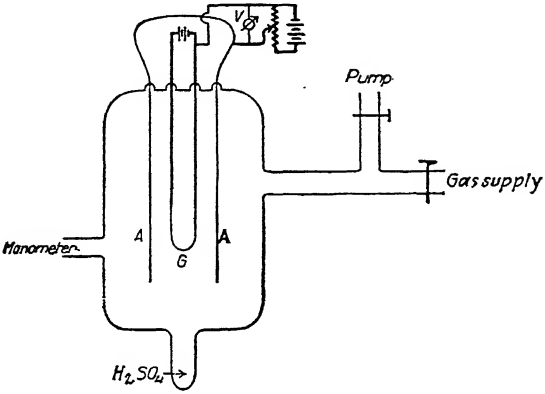

FIG. 109.

The experimental arrangement (Fig. 109) is very simple. The reaction chamber, into which the mixture of the pure component gases is introduced under a total pressure of several tenths of a millimeter, contains an incandescent tungsten filament *G* which serves as the electron source (cathode); anodes *A* of platinum are suspended on both sides of *G*. It was possible to increase gradually the potential *V* applied between the cathode and anode and to adjust the current. The electron stream was held constant at 1–2 milliamperes. The gases were mixed in the ratio $N_2 : H_2 = 1 : 3$ (i.e., in the stoichiometrical proportions). A sensitive manometer connected to the reaction chamber served to detect the chemical reaction ($N_2 + 3H_2 \rightarrow 2NH_3$) by registering a decrease in pressure as the ammonia is formed; an extension tube, blown into the bottom, contained concentrated sulphuric acid to absorb the ammonia as it is produced.

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[2] The heat developed during the action $N_2 \rightarrow N + N$ is not known exactly.

Figure 110 is a time-pressure diagram indicating the variations in pressure with time; the accelerating potential V—in this instance 25 volts—was applied after 20 minutes, the filament G having previously been heated to a very high temperature. During this interval (5–20 minutes) a slight increase in pressure sets in, due, obviously, to disengagement of gas at high temperatures from the heated parts of the vessel; in any event, this pressure increase is not attributable to the formation of ammonia (NH_3) because of the high temperature of the filament.

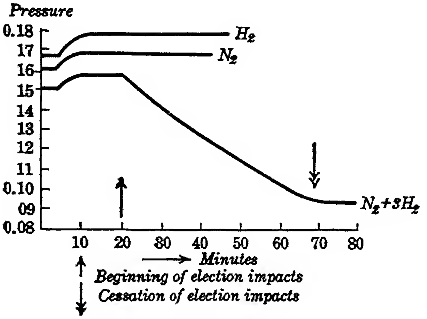

FIG. 110.

The reaction commences only upon the application of the potential, the pressure showing a progressive decrease (as would be expected from the reaction $N_2 + 3H_2 \rightarrow 2NH_3$). The accelerating potential was withdrawn after an interval of 70 minutes and immediately there was a cessation in the chemical reaction also (as is apparent from the horizontal character of the curve for time intervals greater than 70 minutes).

The secondary initial pressure increase was observed likewise when the reaction chamber was filled with hydrogen or with nitrogen alone; however, no effect was evident upon application of the potential. In other words, no change was induced by the electron-stream in the gas content of the chamber.

Having thus established the formation of ammonia (NH_3) by electronic impact, the determination of the critical electron-velocity follows directly. The extent of ammonia-formation with time, i.e., the reaction velocity, was likewise measured in these experiments.

Figure 111 will aid us in our discussion of these data.

Variations in the accelerating potential between the incandescent cathode and the platinum anodes are represented as abscissæ against pressure changes per minute as ordinates. The reaction begins at an electron-velocity of approximately 17.5 volts, the velocity reaction increasing rapidly with increased potential up to about 21.5 volts. For still greater increase in potential, the reactivity increases steadily although there are sharp breaks in the curve characterized by marked maxima and minima. The distance between successive maxima is about 4 volts. Their occurrence has not yet been explained, although it has been suggested that they are related in some way to the dissociation of the hydrogen molecule (H_2) which requires 4 volts, somewhat in the manner that Franck and Cario have demonstrated the dissociation of hydrogen by means of activated (excited) Hg-molecules (see Chap. XXVIII).

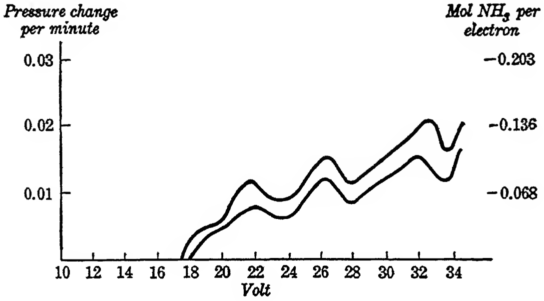

FIG. 111.

It is worthy of mention that the reaction velocity is greatest when there is considerable excess of nitrogen. The yields of ammonia are rather considerable in such cases. In Figure 111, they are indicated as a scale of ordinate along the right edge of the diagram. Thus, for 10 electrons there results (with a potential of 36 volts) the formation of one molecule NH_3—a very good yield for such a reaction, which may even be improved, as is evident from the slope of the curves.

This one example shows that it is well worth the while to carry out more extensive quantitative experiments on gaseous reactions under the influence of electronic impact.

The reactions taking place in Geisler tubes pertain to this problem of chemical action induced by electronic impact, as does also the formation of compounds that are unknown in ordinary chemistry, produced under the influence of electric discharges; and, finally, we have the problem of the possibility of forming compounds of the inert gases. In so far as the former have acquired chemical importance, they are performed in apparatus resembling ozonizers. The presence of complex chemical reactions in Geisler tubes is demonstrated by the change in the form of the discharge and in its structure, as gas mixtures are introduced into the tube. However, systematic experiments dealing with the phase of our subject are not known to the author. In the second group we may place those metallic combinations likewise recognizable in vapor arc lamp, etc., by their band-emission, which give evidence—at least of a transitory character—of the existence of molecules constituted of excited atomic states and of normal atoms. Mention was made likewise of molecules of the inert gases. The possible occurrence of molecules of this type is proven by the respective spectra of these gases; specifically the existence of an (He-He) molecule is established beyond all doubt. In any event, the activated atomic state of helium, which, to all appearances, is involved in this combination (He-He), obviously is of a peculiar nature, similar to the so-called "metastable states" of Franck. Metastable states are characterized by the fact that they may be produced from a normal atom by electronic impact exactly as are other activated states, but they are differentiated by their inability to revert to the initial state with an attending radiation; they remain intact, however, until they revert spontaneously into the normal form of the atom as a result of collisions with other atoms, the reversion taking place with a disengagement of energy (as kinetic energy, thermal energy) but without a concurrent emission of radiation. Impacts which do not bring about such a reversion—their character is not yet quite intelligible—can thus give rise to formation of molecules. He_2-molecules, obviously, are of this type, such molecules having been recognized spectroscopically.

Indeed, we may expect this activated metastable state of helium to be especially reactive inasmuch as the theory of spectral lines and Bohr's theory of atomic structure both ascribe to it an alkali-character; i.e., a metastable atom of He should possess a characteristic alkali configuration. As a fact, self-subsisting compounds of mercury and helium, investigable by physical-chemical methods, have been prepared recently by gaseous discharges in mixtures of helium and mercury vapor (J. J. Manley, Nature, 1925, p. 337). As indicated by G. Joos (Naturwissenschaften, 1925, p. 697), such a compound should prove very high in energy content, i.e., a highly explosive (unstable) compound; it is possible, therefore, that so much energy is liberated during compound formation, because of a peculiar mode of combination, that a rather stable "helide" may be formed. K. F. Bonhoeffer has suggested a method—based upon the data gathered by R. W. Wood on electric discharges in hydrogen—to utilize the highly reactive atomic states arising in Geisler tubes in chemical reactions outside of the tubes. Wood sought the conditions under which electrically stimulated hydrogen will no longer emit the molecular spectrum but only the atomic spectrum. He found it necessary to use discharge tubes of great length since the atomic hydrogen produced by electronic impact obviously is catalytically combined to H_2 in the neighborhood of the electrode. He succeeded in showing that atomic hydrogen was characterized by a rather extended "life-period" in the absence of metallic surfaces: with efficient pumps this atomic hydrogen was easily withdrawn from the discharge tube.

Wood demonstrated that a tungsten wire placed in a long Geisler tube modifies the spectral emission in its vicinity, the line spectrum being transposed to a band spectrum. The tungsten wire simultaneously became incandescent, obviously due to the absorption of the dissociation energy D, about 90,000 cal. released during molecule formation,

$$H + H \rightarrow H_2 + D.$$

Incandescence of a tungsten wire was also noted in the side tube several centimeters away from the discharge tube, through which the hydrogen is pumped out of the discharge tube. This observation served as the basis for K. F. Bonhoeffer's investigations on "active hydrogen," i.e., atomic hydrogen.

We shall first consider briefly why atomic hydrogen should have such a large life-period, and why such an atom does not recombine upon impact with other hydrogen atoms to form a H_2-molecule, even without the presence of a metal. An answer to these problems, based on quantum theoretical considerations, was proposed by K. F. Herzfeld (later extended by Born and Franck). Their reasoning is somewhat as follows: when two atoms unite to form a molecule, the dissociation energy necessary to decompose the compound is set free. For this to be a stable union, some other body must be present to accept this evolved energy from the newly formed molecule. They assume, accordingly, that a H_2-molecule formation can occur only when three atoms simultaneously impact against one another: two of these colliding atoms will unite to H_2, while the third accepts the released energy of formation ($H + H \rightarrow H_2$) as kinetic energy. Loss of H-atoms may occur still in another way, viz.: by formation of H_3-molecules, although we merely know—from the experiments of Landauer and Wendt—that this easily liquifiable and rather reactive (reducing) combination exists. This second "active" hydrogen must not be confused with Bonhoeffer's atomic H-reactions.

A short outline of Bonhoeffer's experimental arrangement follows, (Fig. 112). The discharge vessel of several meters length is operated under a potential of several thousand volts, direct or alternating current. Atomic hydrogen (mixed with molecules!) is drawn off at the left, while equal quantities of H_2-hydrogen are introduced into the discharge tube at the right. Various substances are placed in the reaction chamber, among them being the chlorides of copper, lead, bismuth, mercury, the sulphides of cadmium, copper, mercury, the fluorides of copper, silver, etc. All these compounds were reduced to the metallic state; oleic acid was hydrated. A very interesting phase of this problem is to determine what metals—and, likewise, their condition—are capable catalytically to transpose atomic hydrogen into molecular hydrogen. Experiments of a qualitative character on the velocity of reconversion without catalyst are already available: they decidedly favor Herzfeld's assumption that a simultaneous impact of three atoms is necessary for molecule formation.

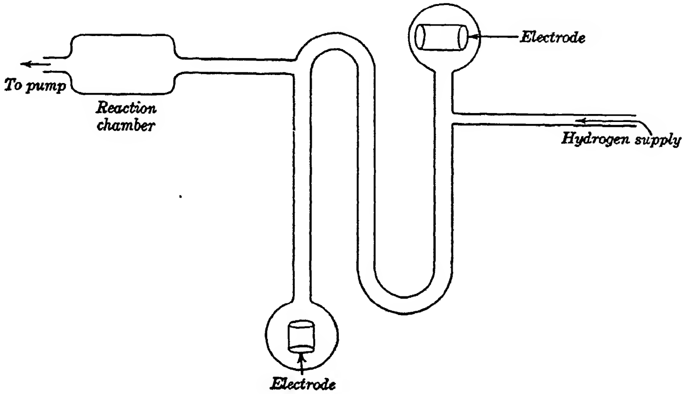

FIG. 112.

Without a doubt, these results indicate the feasibility to press into service the variations in the physical states of the atom, for the performance of chemical work.

CHAPTER XXVIII

PHOTOCHEMICAL CATALYSIS

We shall here formulate the results of Chapter XXV in a somewhat different manner—as chemical reactions. A mercury atom is illuminated with a radiation of frequency ν which is absorbed by the atom. The quantum energy of this radiation—wave-length is 2,536.7—is $h\nu_{\mathrm{Hg}}$; the Hg-atom is transposed into the higher energy state with absorption of this energy,

$$\mathrm{Hg} + h\nu_{\mathrm{Hg}} = \mathrm{Hg}'; \tag{1}$$

in the absence of disturbing influences the reversal of this action takes place spontaneously following an average life-period of the excited Hg′-atom of about 10^{-7} seconds,

$$\mathrm{Hg}' \rightarrow \mathrm{Hg} + h\nu_{\mathrm{Hg}}, \tag{2}$$

the previously absorbed energy being liberated in the same form and quantity. This phenomenon is termed "Resonance." If, however, the activated mercury atom Hg′ collides with an atom of another element, e.g., a thallium atom, reactions (3*a*) and (3*b*) may take place instead of reaction (2): thus

$$\mathrm{Hg}' + \mathrm{Tl} \rightarrow \mathrm{Tl}' + E + \mathrm{Hg}, \tag{3a}$$

$$\mathrm{Tl}' \rightarrow \mathrm{Tl} + h\nu_{\mathrm{Tl}}. \tag{3b}$$

These actions will take place only if the difference in the energy contents of the two mercury states is greater than the difference between the two thallium states, i.e., if $(\mathrm{Hg}' - \mathrm{Hg}) > (\mathrm{Tl}' - \mathrm{Tl})$; E is the difference of the two energies and probably appears as kinetic energy. (3*a*) and (3*b*) depict the results of Cario's experiment described in Chapter XXV. By a combination of reactions (1) and (3*a*) we can express this as follows: a normal thallium atom may be transformed photochemically into an activated thallium atom by means of mercury as a catalyst.

A number of chemical reactions are known that proceed through the instrumentality of "photo-catalysts." The question therefore presents itself: can the corresponding energies requisite for other reactions also be imparted to the reaction components by means of such a photochemical process? In selecting a definite reaction for investigation, it must be borne in mind, naturally, that the reaction energy cannot exceed the radiation energy imparted to the catalyst.

A particularly interesting problem is offered in the work of dissociation of hydrogen, i.e., in the energy necessary to disrupt the H_2-molecule into its two atoms, which collectively contain more energy than does the molecule H_2. Thermal experiments have determined this dissociation work to be about 90,000 cal. pro mole of hydrogen—values range from 70,000 to 100,000 cal. If this energy be denoted by Q, we will have

$$H_2 + Q \rightarrow H + H.$$

All attempts to impart this necessary energy Q to the hydrogen molecule as electronic energy have proved futile. The hydrogen molecule does not accept the corresponding electron energy of 3.5 volts; 3.5 volt electrons penetrate hydrogen without losing their energy during collisions with molecules. In other words, they fail to dissociate hydrogen. If the volt-velocity is increased—i.e., with increasing electron energy—it becomes apparent that dissociation cannot be accomplished in this manner. There first forms an activated molecule H_2', and subsequently an ion H_2^+, as may be concluded, on the one hand, from direct measurements and on the other hand from the observed spectrum of the H_2^+ ion. Radiation is equally ineffective in producing dissociation even when the energy quantum $h\nu$ of the illuminating radiation is taken equal to the work of dissociation (λ is approximately 3,000 Å.): obviously the hydrogen molecule does not absorb this radiation energy; hydrogen is permeable even to the extreme ultra-violet.

It seemed feasible, therefore, to attempt an experiment in which hydrogen molecules would come into direct contact with activated mercury atoms whose energy difference over and above the energy content of the normal state assuredly is greater than the energy requisite for the dissociation of the H_2-molecule, viz.: 120,000 cal. as opposed to about 90,000 cal. This experiment was undertaken by Cario and Franck.[1] The anticipated result was fully realized, viz.: the photochemical dissociation of hydrogen by means of mercury as a "photo-catalyst." The reaction-mechanism may be formulated as follows:

$$H_2 + Hg + h\nu_{Hg} \rightarrow H_2 + Hg' \rightarrow H + H + Hg + E_{Kin.}$$

The inclusion of the end-term $E_{Kin.}$ in this equation is necessary inasmuch as the equation should not only embody the primary and secondary reaction products but be correct also from the energy point of view. The term $E_{Kin.}$ comprises the excess energy not utilized by the Hg'-atom in bringing about the dissociation of hydrogen. Other experiments by Franck and Cario have demonstrated that this energy becomes evident here also as kinetic energy of the reaction products. The production of hydrogen atoms was established by the reduction of CuO and of WO_3; furthermore, the production of water was likewise evidenced during the reduction process. We have here an instance, therefore, of a catalytic reaction in which the mechanism of catalysis may be attributed to known physical facts and which is explainable by means of convincing experimental evidences.

This experiment is of especial interest for the theory mentioned. It is known that the reaction $Hg' = Hg + h\nu$ (resonance radiation emission) will proceed quantitatively only when the activated atoms previous to emission are not disturbed by collisions with other atoms to such an extent that they lose their capacity to radiate. The resonance capacity of mercury is utterly destroyed even at very small pressures if increasing quantities of water are introduced into

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[1] G. Cario and J. Franck, Zeitschr. f. Phys. 11, 161 (1922).

mercury vapor; whereas the absorption of the exciting radiation does not decrease in anything like the same amount. Since mercury atoms likewise absorb the same energy at higher pressure of admixed gas, it follows that the Hg′-atoms, formed by radiation, must lose their energy in a manner other than by radiation. We do not know just how this energy destruction takes place in each individual case, as, for example, during addition of an inert gas from which all chemical reaction is excluded. It may be, however, assumed that the energy is evolved in the form of radiation, although in smaller quanta, e.g., as infra-red radiation. In the particular case under discussion, the admixture of hydrogen to the mercury vapor, this energy is utilized to effect dissociation of the hydrogen molecule. The mutual compensation of the processes, resonance-extinction and dissociation, is evident from the dependence of both effects on pressure; with decreasing resonance radiation the dissociation yield will increase, reaching a maximum constant final value at the pressure at which the resonance-capacity has been completely destroyed. The lower portion of Figure 113 depicts the decrease in intensity of the resonance radiation with pressure; the upper part shows the increase of dissociation of the hydrogen molecule as measured by the decrease in pressure per minute brought about by the withdrawal of H-atoms formed during the dissociation.

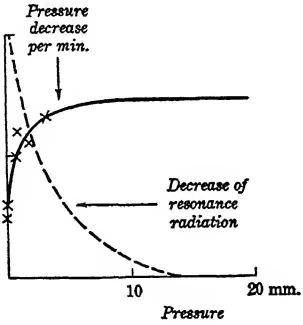

FIG. 113.

J. Franck has applied this mechanism of photochemical catalysis to the elucidation of other processes, among them being the sensitization of the ordinary photographic dry plate. The photographic process, as already discussed in our considerations on normal photochemistry in Chap. XXIV, consists essentially in the disruption of an AgBr molecule as a consequence of light absorption. Only a very small energy amount is necessary to accomplish this disruption; very large wave-lengths should therefore suffice for this action. Experiment has demonstrated, however, that a photographic plate of AgBr emulsion is sensitive only to wave-lengths of 5,000 Å. to shorter waves. The objective reason for this is very readily determinable: radiation of longer wave-lengths is not absorbed, and consequently it cannot become effective. It has been known for quite a long time that admixture of dye-stuffs to the emulsion, for example, dipping the plate in a dye solution, "sensibilizes" the photographic dry plate for certain wave-length ranges. These are the wave-length ranges that are absorbed by the respective dye employed. According to Franck, sensitization of the silver bromide consists in the absorption of the radiation by the dye-stuff, that is, it absorbs the radiation energy. The normal dye-stuff molecule M is thereby transposed into a more energetic molecule M' which, in turn, releases its energy to a silver bromide molecule when it "collides" with the latter because of the close packing of the molecules. The sensitization mechanism may accordingly be represented in a manner analogous to dissociation of hydrogen:

$$M' + \mathrm{AgBr} \rightarrow M + \mathrm{Ag} + \mathrm{Br}.$$

The light-resistance, or lack of such, on the part of dye-stuffs, must be understood in this sense. The dye-stuff absorbs light energy, and is transformed into another molecular state. This, in turn, impacts its energy to the dyed material which is thereby changed chemically and thus induces on its part another chemical change in the dye. All the known peculiarities of the non-resistance to light may be included in this formulation: as, for example, the destruction of a dyed material of a definite kind, whereas material of a different type is not affected injuriously and the non-resistance to light of a dye-stuff on one body (fundament) and the "light-resistance" of the same dye-stuff on another body.

CHAPTER XXIX

Radiation Measurements

A theoretical and experimental problem of modern physics, whose intimate relationship to atomistics is not quite evident at first glance, is the radiation of black bodies. A "black" body is defined as a body that will absorb all radiation incident upon it. The black body itself emits a radiation whose total intensity as well as its distribution in the individual wave-length ranges of its spectrum depend solely upon its temperature. Total radiation of a black body may be expressed in the Stefan-Boltzmann law, according to which the total radiation S is proportional to the fourth power of the absolute temperature; or $S = \sigma T^4$, where σ is a constant, known as the Stefan-Boltzmann constant. The radiation energy which a black body of temperature T_1 may thus receive from another black body of temperature T_2 is equal to the difference in radiation of the two bodies: this may be formulated as $K\sigma(T_2^4 - T_1^4)$, wherein K is a constant depending solely upon the geometric arrangement of the two black bodies, i.e., their relative radiating surfaces and their mutual distance from one another. σ designates the radiation emitted in a second by a black body of unit surface and temperature $T = 1°$ abs. at temperature $T = 0°$ abs.

The distribution of the energy over the individual wave-lengths of the spectrum has been solved theoretically by M. Planck by introducing an entirely new viewpoint: the concept of the quantum theory of a definite atomistics of energy. Relinquishing the principle of the equipartition of energy over the degrees of freedom of a system, the quantum distribution of the elements of energy is introduced. As is known, this is the beginning of the quantum theory whose successes have been impressed upon us during the course of the preceding pages. However, the significance of the radiation laws as applied to atomistics is not founded in this alone. The constants appearing in the radiation laws which are directly measurable experimentally bear a numerical, i.e., definitely expressible, relation to the other atomistic constants. Inasmuch as these latter constants are likewise susceptible of experimental measurement, it is evident that a comparison of the experimentally determined radiation constants with the calculated values based on atomistic data and theories is of utmost significance. Furthermore, the fundamental constant of all modern physics—Planck's constant, or the so-called universal constant h—is common to both theories and calculable independently from either set of data.

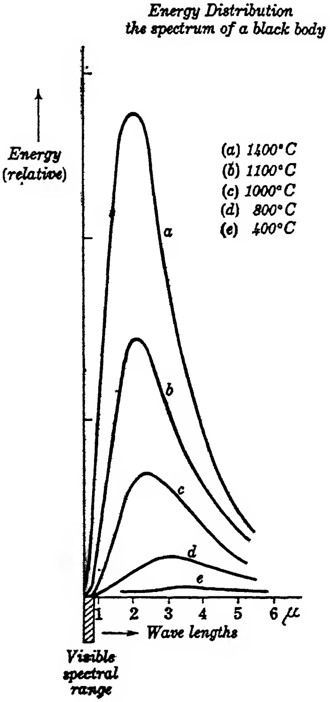

Fig. 114.

According to Planck's law the energy of a wave-length λ in the spectrum of a black body of absolute temperature T is expressible as

$$E_\lambda = c_1\lambda^{-5}\cdot\frac{1}{e^{c_2/\lambda t}-1},$$

and the total radiation for the entire spectrum is expressible as

$$\int_0^\infty E_\lambda d\lambda = \sigma T^4.$$

The above Figure 114 reproduces the energy curves of black radiation for a few temperatures. The sudden and sharp slope on the short waved side of the spectrum conditions the striking increase in brightness with increase in the temperature. In this region, i.e., when the factor T is small, Planck's formula becomes identical with Wien's equation which has proved useful in practical pyrometry, the optical measurement of temperature; under such conditions $E_\lambda = c_1\lambda^{-5}e^{-(c_2/\lambda t)}$. In the long waved region, on the other hand, the radiation energy increases, for a given wave-length, proportionally to the absolute temperature of the radiation, as is apparent from Planck's formula for large λT values: $E_\lambda = e_1{}^{\lambda-5} \cdot \lambda T$ (Rayleigh-Jeans law). This suggests the possibility to test the temperature scale: for long waved monochromatic radiation—obtainable according to the "rest ray" method—energy is measured as a function of temperature; for constant wave-lengths, energy is directly proportional to the absolute temperature. Rubens and Michel performed this experiment in 1921 in which it was found that the temperature scale of the "Reichsanstalt" (Imperial Institute) can be in error at most to the extent of 5 degrees on the basis of the melting point of gold. According to radiation measurements, the melting point of palladium (1,557°) may be 2–3° higher than the temperature recorded by the Imperial Institute, although the latter is about 8° higher than the previously accepted standard value of Day and Sosman.

The constant σ of the total radiation law $\int_0^\infty E_\lambda d\lambda = \sigma T^4$ to which attention has already been drawn, and the constant c_2 in Planck's law $E_\lambda = c_1\lambda^{-5}(e^{c_2/\lambda T} - 1)^{-1}$ of the energy distribution in the wave-lengths λ in the spectrum of a black body of absolute temperature T, are ordinarily designated as "radiation constants."

In the last (Planck's) equation the constants c_1 and c_2 are equal respectively to the values c^2h and ch/k, where c is the velocity of light in a vacuum, h the so-called Planck's constant and K[1] Boltzmann's entropy constant. Of these, c_2 alone has been determined experimentally, thus making h calculable. c_2 may be determined likewise from Wien's displacement law

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[1] Boltzmann's constant can be designated as the gas constant per molecule, viz.: $K = R_0/N$, R_0 being derived from P_0V_0/T and N being Loschmidt's Number, i.e., the number of atoms per gram atom. N is derivable from the electro-chemical equivalent Q and the elementary electric quantum, according to the relation $N = Q/e$. Numerically $K = 1.371 \times 10^{-16}$.

according to which the wave-length of the maximum radiation intensity is related to the absolute temperature according to the relation

$$\lambda_{\text{max.}} \cdot T = b = \frac{c_2}{4.9651} = \frac{ch}{K \times 4.9651}.$$

The first "radiation constant," σ, is directly determinable experimentally or it may be computed from Planck's law by integrating, from which

$$\sigma = \frac{48\pi\alpha K}{c_2{}^3} = \frac{48\pi\alpha K^4}{c^3h^3},$$

where α is the numerical factor $\pi^4/90 = 1.0823$.

We observe therefore that the value of the universal constant h is derivable from c_2 and σ. The magnitude h, on the other hand, is directly determinable from the quantum theory of atomic structure and of spectral lines. A relationship is thus suggested between the several constants. It is apparent furthermore that the quantum theoretical calculation of h involves still another atomistic constant, the magnitude ϵ, the elementary quantum of electricity. This latter constant may be regarded as the most definitely known and exact atomistic constant, its magnitude 4.774×10^{-10} electrostatic units being uncertain to the extent of only a few parts per thousand.

Further important numerical relations exist between the elementary quantum, the radiation constants and the spectroscopic constants—that is, Rydberg's constant and the constant of fine structure. (For further details the reader is referred to Landé, Wissenschaftliche Forschungsberichte, vol. V.)

We will consider briefly the experimental determination of the radiation constants. The Stefan-Boltzmann constant, whose validity for wide temperature ranges has been demonstrated for a long time, is determined by the absolute measurement of the radiation emitted by a black body of temperature T (the "radiation") and radiating surface F_1 to a second black body at a lower temperature T_2 ("receiver") and a "receiving" surface F_2, at a distance r. This may be expressed

$$S = \frac{\sigma}{\pi} \times \frac{(T_1^4 - T_2^4)F_1 \cdot F_2}{r^2}.$$

The absolute measurement of σ was first carried out in a precise manner by W. Gerlach, using the absolute thermopyle method (F. Paschen). In this method the "receiver" consists of a very thin, thoroughly blackened metallic strip, which becomes heated by the incident radiation. Its temperature rise is recorded by means of a large number of thermoelements, whose soldered joints are (arranged) placed against the rear of the ("receiver") strip. The radiation is then screened off, and an electric current sent through the metallic strip until the same temperature rise—heating effect of the current—is registered by the thermopyle. Under such conditions, obviously, the "Joule" heat produced in the strip is equal to the radiation S absorbed by it. Or

$$S = J^2 w = \frac{\sigma}{\pi} \frac{(T_1^4 - T_2^4)F_1 F_2}{r^2}.$$

From the several measurable magnitudes, the radiation constant may be evaluated as 5.75 ± 1 per cent $\times 10^{-12}$ watt cm.$^{-2}$ degree^{-4}. This value must be increased about 1 per cent inasmuch as the blackened strip (receiver) does not totally absorb but reflects about 1 per cent of the incident radiation, the heating effect due to the absorbed radiation being too small by this amount. It is important also that the pressure of absorbing gases (water vapor and carbon dioxide) be eliminated from the space between the "radiator" and "receiver," since even small quantities of such gases absorb considerable amounts of infra-red radiation. In Gerlach's experiment this correction factor was measured directly. From his data, the value of σ is found to be $\sigma = 5.80 \times 10^{-12}$ watt cm.$^{-2}$ degree^{-4}.

Measurements made by Coblentz in America are in fair agreement with this value. Coblentz employed apparatus essentially similar to that of Gerlach. At the suggestion of H. Rubens the Stefan-Boltzmann constant was redetermined recently by two other methods; these experiments likewise confirm with great accuracy this value of σ. Sonvico measured the radiation of a black body by means of an ice-calorimeter prepared as a black body. The value of σ, as communicated by H. Rubens, was 5.75×10^{-12}, the records of the experiments having been lost during the World War. Subsequent experiments were undertaken by A. Kussmann; these experiments are especially important as a confirmation of Gerlach's method. Kussmann finally modified the experimental arrangement by focussing the heat, produced in the metallic strip alternately by the incident radiation and by the electric current, upon the soldered joints of a micro-radiometer by means of a rock salt lens. In this wise certain errors of the thermopyle method were avoided. The result of these experiments—due regard being given to absorption and reflection losses—was 5.795×10^{-12}, in exact agreement with Gerlach's value. Finally, Hofmann (likewise under Rubens' direction) determined the Stefan-Boltzmann constant to be 5.76×10^{-12} according to the method of Shakespear-Westphal (electric compensation of the heat liberated by a black body by radiation in vacuum). The value $5.75 - 5.80 \times 10^{-12}$ watt cm.$^{-2}$ degree^{-4} may be considered as known exactly within 1 per cent.

Two different methods are available to determine the radiation constant of Planck's law: the measurement of the radiation intensity as a function of the wave-length at constant temperature ("Isotherm-method") and, secondly, the determination of the intensity of radiation as a function of temperature at constant wave-length ("Isochromatics"). The most reliable measurements are due to Warburg and to Rubens and Michel,[1] the latter having dispelled the doubt—due to Nernst—of the validity of Planck's law. Of interest also in this connection is the investigation recently carried out in the ultra-violet region by E. Steinke [2] by means of a

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[1] Zeitschr. f. Phys. 9, 285 (1922); Berl. Ber. 1921, 590. Contains a bibliography.

[2] E. Steinke, Zeitschr. f. Phys. 11, 215 (1922).

photo-electric method, previously undertaken by E. Baisch photographically.

We may accordingly accept the following numerical values of c_2 as equally probable:

$c_2 = 14{,}250–14{,}350$ (Warburg and coworkers),
$c_2 = 14{,}275$ (Michel and Rubens and Michel).

For calculations in practical photometry and pyrometry, the value 14,330 is commonly employed in America, and 14,300 in Germany.

This will yield for the constant of Wien's displacement law the value $b = 0.2875$ cm. grad. and for the constant h (taking $\sigma = 5.80 \times 10^{-12}$), $h = 6.54 \times 10^{-27}$ erg sec.

This value is in marked agreement with the value determined from direct quantum relations of photo-excitation, from the photo-electric effect and for Roentgen ray excitation: $h = 6.51 - 6.56 \times 10^{-27}$ erg sec. It is likewise in accordance with the value calculated from known spectroscopic data by Sommerfeld: $h = 6.526 \times 10^{-27}$ erg sec.

This numerical concordance accentuates, beyond the power of words, the correctness of the principles upon which are based all our atomistic and quantum theoretical conceptions.

Of practical importance, we may mention, here, the absolute measurement of the total radiation of a Hefner-lamp, whose radiation is adopted as the photometric norm. This has been measured under exactly defined conditions:[3] $S = 0.225 - 0.230$ gram-cal., that is, the Hefner-candle radiates this amount of energy per second through a square centimeter at a distance of 1 meter. This value is taken as a standard for the calibration of thermopyles, bolometers and similar instruments. The slight dependence of total radiation upon exterior factors (in contrast to optical luminosity) is discussed in detail in the original publications. The mechanical equivalent of photo-radiation of the Hefner-lamp, i.e., of the "Hefner-candle," may be computed from the

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[3] W. Gerlach, Physik. Zeitschr. 1913 and 1920.

measured absolute total radiation and the photo-radiation measured on the same scale. Since photo-radiation is 9/1,000 of the total radiation, the equivalent becomes equal to 0.227 × 0.009 = 0.00204 gr. cal. = 85,000 ergs.

Furthermore, for practical photometric purposes it is essential that we know the radiation characteristics of the incandescent metal, i.e., we must have knowledge of the total radiation law $S = \gamma T^n$ (for black bodies, $\gamma = \sigma$, $n = 4$) and of the energy distribution law $E = f(\lambda, T)$. Of the numerous available measurements we may cite platinum as an example of a metal which is characterized by a simple radiation law. The recent measurements by Geiss are given: $J = \epsilon \cdot \sigma T^4$, from which the portion ϵ of the total radiation σT^4 of the black body may be evaluated as

$$\epsilon = 6.22 \times 10^{-4} T^{0.767} \text{ watt cm.}^{-2}.$$

This simple relation between black radiation and platinum radiation,

$$S_{\mathrm{Pt}}/S_{\mathrm{S}} = \epsilon = 6.22 \times 10^{-4} T^{0.767},$$

is valid between 200° and 1,300° C.

Radiation Pressure

The uncertainty that has gradually characterized our long accepted conceptions of the radiometer effect and the properties of the radiometer because of newer experimental observations necessitated, likewise, a repetition of the experimental measurement of radiation pressure, first carried out in 1900 by P. Lebedew according to the radiometric method. The later experiments of Nichols and Hull no longer could be regarded as conclusive inasmuch as their method makes use of an anomaly—whether rightly so, or not, cannot be determined—of the radiometer in order to eliminate heat effects. Moreover, the modern development of high vacuum technique makes it possible to undertake measurements in much higher vacua than were available to Lebedew. Although our knowledge of the radiometer effect and of other forces influencing the turning moment of the radiometer is very indefinite and uncertain, one thing is fairly well established, viz.: that these several effects are results of gas molecules. It was necessary, therefore, to produce very high vacua definitely to eliminate disturbances due to gas-effects. Such vacua were attainable by means of Vollmer's high vacuum pumps and by cooling in the presence of cocoanut charcoal for days by means of liquid air. The rotatory system of platinum (or other metal) vanes of about 1 square centimeter was suspended by means of a long thin quartz fiber in a large spherical flask with plane, occluding plates. The deflection produced by the incident light was noted by means of a mirror scale. The direction-force of the threads was about 10^{-3} dyn./cm.; the sensitivity of the torsion balance was $2–7 \times 10^{-7}$ dyn./cm. per mm. of the scale division. The

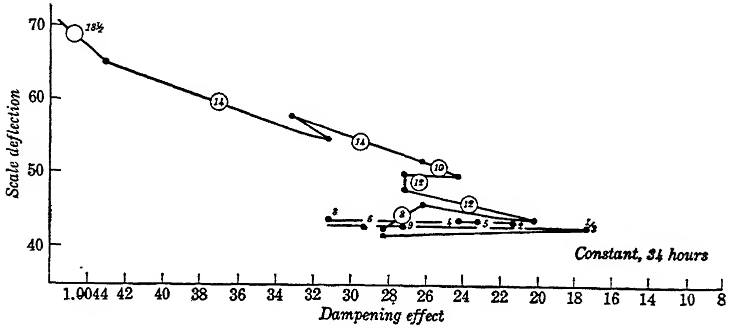

FIG. 115. Platinum:—First series of measurements.

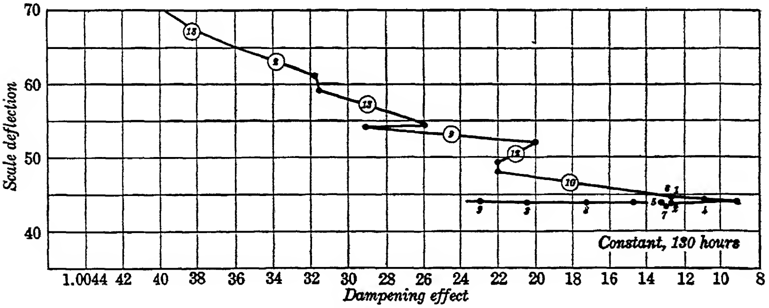

FIG. 116. Platinum:—Second series of measurements.

vessel was evacuated while subjected to a continuous radiation. The radiometer curve was then taken. After days of pumping, the deflection of the system became independent of the pressure and proceeded—as is indicated by the absence of inertia effects—without thermal disturbances. Three examples are reproduced in Figures 115–117: in each case, ordinates represent deflections of the torsion balance for constant illumination, and abscissæ the damping relation of the system, given as a measure of the decreasing pressure (of the order of 10^{-6} to 10^{-7} mm. Hg). The numbers inserted along the curve designate the time in hours elapsed between successive measurements during which intervals the vessel was continuously evacuated.

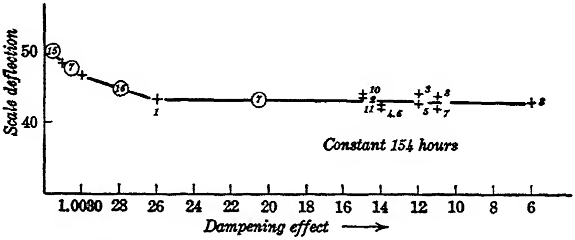

FIG. 117.

Vane Material	Calculated Radiation Pressure	Observed Radiation Pressure	Difference, Per Cent
Platinum 7 μ	3.24×10^{-5}	3.12×10^{-5}	− 4
	3.24×10^{-5}	3.15×10^{-5}	− 3
	1.49×10^{-5}	1.44×10^{-5}	− 2.5
Nickel 10 μ	3.05×10^{-5}	3.23×10^{-5}	+ 6
Aluminium 15 μ	3.86×10^{-5}	3.89×10^{-5}	+ 1
	3.86×10^{-5}	3.94×10^{-5}	+ 2
	1.68×10^{-5}	1.74×10^{-5}	+ 3

The radiation pressure may be calculated according to the Maxwell-Bartoli formula

$$p = \frac{E}{C}(1 + \rho),$$

wherein E designates the absolutely measured radiation energy, c the velocity of light, and ρ the reflectivity of the illuminated surfaces. The radiation energy was of the order 10^5 to 10^6 erg per sq. cm. The theoretically computed pressures were duplicated with an accuracy of a few per cent.

The data of the above table give evidence of the experimental confirmation of the theoretically anticipated radiation pressure.

CHAPTER XXX

ATOMISM AND MACROCOSMOS

In this concluding chapter we will discuss an entirely novel and especially interesting application of the modern theory of the atom, viz.: the attempt to explain the physical conditions of fixed stars by means of their spectral emissions. It is known that the emission and absorption spectra of stars permit a chemical analysis of their constituents, just as a study of the spectrum of a luminous gas or of a luminous vapor is utilized in the laboratory for a chemical analysis of the atom emitting the light. It must be remembered, however, that masses heated to very high temperatures do not only emit a line spectrum. As already remarked in the chapter on radiation measurements, the emission of a solid body is of a somewhat different character: it consists of a continuous spectrum. Such a spectrum, however, is emitted not only by solid bodies as such, but—as is indicated by the experiments of F. Paschen—by gases also, provided they radiate in sufficiently dense layers; layers of appropriate thickness are present, without a doubt, in stars. As a matter of fact, we observe a continuous spectrum in addition to the absorption and emission line spectra of stars; but its existence reveals nothing to us about the structure of stars beyond the fact that stars consist of highly heated masses; in other words, it fails to inform us whether these masses are present in the solid, liquid or gaseous condition. These two spectra are all that the star imparts to us, and it devolves upon us, accordingly, first to investigate the physical conditions under which emissions of this type are produced, and subsequently to draw conclusions regarding the physical conditions of the stars.

We will first review the available physical knowledge that may prove helpful to us in this astral-analysis.

1. The spectrum of a luminous mass depends solely upon its temperature. In the chapter on radiation measurements it was noted that the absolute measurement of the total radiation as well as the measurement of the energy distribution in the continuous spectrum make possible the direct determination of the temperature of the radiating body.

2. It is known since the time of Kirchhof and Bunsen that the selective emission of an atom is characteristic of it; the chemical nature of a given body is definitely recognizable from the line spectrum of its luminous gas or vapor. Physical research, i.e., modern spectroscopy, however, has pointed out that this by no means exhausts the capabilities of spectral analysis. Thus, it was found that the illumination emitted by an atom, its spectral emission, is characteristic not only of its chemical nature, but of its physical condition as well. One and the same atom can be stimulated to the emission of various spectra; in other words, the chemical atom can exist in several different states or conditions.

3. These several physical states of an atom are differentiated from one another by their respective energy contents. It was observed that it depends entirely upon the extent of the energy imparted which of the possible line spectra of a chemical element will be emitted.

4. Consequently the line spectrum informs us simultaneously regarding the chemical nature and the physical condition of the emitting atom.

5. We know from Bohr's atom theory how line emissions are related to the physical conditions of atoms, the correctness of this relationship having been confirmed by experimental investigation, as already discussed in Chapters XI and XII: line radiation is emitted during the transition of the atom from a higher (a more energetic) state to a lower (low-energy content) state.

6. Impartation of a definite energy amount greater than that requisite for photo-excitation ionizes the atom. The ionized form is thus a more highly energized state of the

normal atom. Furthermore, the ion may likewise be elevated to still higher energy levels by the addition of more energy, i.e., it too may be stimulated to the emission of line radiations whose series is characteristic of the ion.

7. The spectral emissions resulting from the transitions between more energetic and less energetic states below the ionization stage are commonly designated "flame" or "arc spectra" while the line spectrum of the ion is termed "spark spectrum." This nomenclature is due to the fact that the lower excitation predominates in the flame or in the electric arc whereas in the electric spark the higher excitation is in preponderance. The spectra rarely occur entirely separated or apart from one another. The intensity of corresponding spectral lines can serve therefore as a convenient measure of the number of atoms present in the respective states.

8. The radiation excitation energy and the ionization energy are fundamental constants of the atom.

9. Apart from these atomic constants, the physical condition of the atom depends in thermal equilibrium upon the temperature and the pressure of the emitting layer. This dependence may be formulated according to the laws of chemical equilibrium. If we designate a normal atom by A, and by A' an excited state of it produced by the addition of energy U required to bring about this change, the equilibrium relationship may be expressed as $A \rightleftarrows A' - U$.

10. This equilibrium can be destroyed, however, by electrical forces and by incident radiation. The influence of the latter is especially evident since the transfer of a normal atom into a more energetic or excited state may be accomplished—as was observed in earlier considerations—also by absorption of incident radiation.

11. The width of the emitted spectral lines serves as an important characteristic identifying the particular state of an emitting atom. This width depends essentially upon the pressure, density, thickness and the "chemical" forces present in the radiating layer. The "chemical" forces are electrical effects arising from neighboring atoms: to them we may

attribute primarily the broadening of the spectral lines observed in flames charged with luminous salts or the broadening of absorption lines in non-luminous metallic vapors occasioned by the admixture of gases. We may conceive this widening to result from a derangement of the atomic structure that precedes a chemical molecular union upon the approach of the reacting constituents. A mutual derangement results also upon the close approach of two atoms even though these do not enter into chemical combination with one another.

We have thus summarized in eleven specific fundamental principles many results that have been discussed elsewhere in these chapters, stressing the physically essential facts and disregarding all reference to any special model representations. Before we can attempt, however, to extend these principles to the chemistry and more particularly to the physics of stars, we must consider the essential facts of astronomy and of experimental astro-physics.

I. All fixed stars have approximately the same mass (10^{33}–10^{34} gm.). There are only a few whose mass is tenfold that of the sun (2×10^{33} gm.). Masses equal to 50 times that of the sun are exceedingly rare. This fact, although known for a long time, has been established physically with reference to radiation pressure by means of Eddington's theory [1] of the conditions governing the existence of stars. Fixed stars are differentiated by their size and their temperature.

II. The temperature of fixed stars may be determined experimentally from the energy distribution in their respective spectra. This generalization represents a direct application of Rule 1 of the physical principles enunciated above.

III. The observed total luminosity of a star is not indicative of its temperature or of the light intensity of the star. The luminosity observed here on the earth depends upon the magnitude of the star, i.e., the extent of its surface as well as its distance to the location of the observer.

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[1] We shall not enter into a discussion of this theory. See Eddington, Zeitschr. f. Physik 7, 351 (1922).

IV. If the distance to a fixed star is known, the absolute luminosity or the absolute magnitude may be determined from the observed luminosity and the distance.

V. This absolute $\frac{\text{magnitude}}{\text{luminosity}}$ ratio is related in no way to the temperature of the radiating surface as is indicated by a comparison of the experimental results of II and IV. The extent of surface of the various stars consequently must be different; the absolute luminosity will be the greater, the larger the extent of the radiating surface. Stars may be classified accordingly into

VI. "Giant" stars and "dwarf" stars. There are "giant" stars and "dwarf" stars of equal temperature whose observed luminosities are in the proportion of 10,000 : 1 and whose diameters are of the order 100 : 1 inasmuch as the ratio 10,000 : 1 designates also their relative radiating surfaces. If they have equal masses—according to Rule 1—their densities must be different.

VII. If the luminosity of a star is plotted diagrammatically as a function of its temperature, determined according to II, it will be evident from the resulting curve how the stars which are available for such a comparison (over 2,000)—i.e., stars whose absolute luminosity may be determined from the observed luminosity and the known distance—are classifiable into two groups. A horizontal band will comprise the giant stars, whose quantity of radiation per sec. per gram mass is constant and independent of the temperature.

VIII. Fixed stars show in addition to a continuous emission the line spectra of known chemical elements in absorption.[2] According to earlier views certain elements were noticeably absent, e.g., in the spectrum of the sun. A number of such instances have been explained by the observation that not all the spectral lines of these elements but only the spectral lines of a definitely excited state—e.g., arc or spark lines—were wanting.

IX. The stars are further classifiable according to the type of these line spectra into distinct spectral groups.

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[2] In absorption—as the familiar Fraunhofer lines in the solar spectrum.

X. Spectral classification of stars is a measure of the temperatures of stars. According to generalizations 4–8 of the physical principles we may draw conclusions as to the physical conditions of the stars in which emission takes place; in other words, we may arrive at the nature of fixed stars.

XI. Even more extensive inferences may be drawn from the width of the spectral lines—according to II—regarding the density, thickness, the chemical, the magnetic and the electric forces. However, material of a sufficiently definite character is not yet available.

Thus far the exposition of these several relationships. It is obvious that the application of the principles of atomic physics to the exploration of stars consists in the correlation of the temperature and pressure of the fixed stars with definite excitation energies obtainable in laboratory experimentation and, further, in the comparison of the spectra emitted under these known excitation energies and of the spectra of the fixed stars. Meg Nad Saha was the first to attempt consistent work in this direction. We will choose for discussion two especially clear cases. Hydrogen is known to us as a diatomic gas. At higher temperatures, i.e., upon the addition of energy, it dissociates into hydrogen atoms according to $H_2 \rightleftarrows H + H - U$.

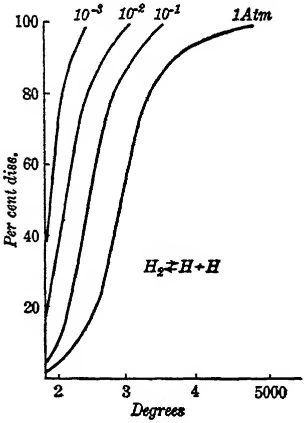

FIG. 118.

U is the dissociation energy. According to thermo-chemical principles, e.g., Nernst law, the degree of dissociation is calculable from its dependence upon temperature and pressure. Figure 118 shows these results diagrammatically. On the other hand, we know that the normal hydrogen atom both emits and adsorbs the familiar Balmer spectral series, the hydrogen lines α (red), β (blue green), γ (blue), δ (violet). The occurrence of these lines in ~~the spectrum of~~ a given star indicates the presence of atomic hydrogen. Upon the addition of more energy, the hydrogen atom is transposed into the H-ion. Inasmuch as the energy requisite for this change is known to us from experiment, we can apply the same considerations to the ionization of the atom that were applied to the dissociation of the molecule H_2; that is, we may formulate the ionization as

$$H \rightleftarrows H^+ + \epsilon - J,$$

wherein J is the ionization energy.[3] The indicated equilibrium will be displaced entirely to the right at a definite pressure and temperature; as a consequence of such a displacement we may anticipate the disappearance of those spectral emissions peculiar to the normal hydrogen H-atom. If, therefore, we observe for a definite spectral class the disappearance of the normal H-lines, we must conclude either that the temperature is too low for dissociation of the molecule H_2 into H-atoms to take place, or the temperature is so high that all the atoms are ionized. The temperature determined from the energy distribution in the continuous spectrum makes possible the correct selection of one of these two alternatives; on the assumption of a pressure, the spectral observation permits one to state the temperature of the star, or at least corresponding sets of temperature and pressure possible for the star in question.

At the disappearance of the Balmer-lines, there can be no more hydrogen lines as such, since the ion of the hydrogen atom, its nucleus, no longer has a "photo-electron," i.e., the ion cannot be transposed into a higher energy state capable of radiation. Ionized hydrogen cannot be detected spectrally —and consequently can not be proved present in stars.

Another example is had in the element calcium, whose absorption lines are especially familiar and characteristic. Thus we have

$$Ca \rightleftarrows Ca^+ + \epsilon - J,$$
$$Ca^+ \rightleftarrows Ca^{++} + \epsilon - K.$$

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[3] J. Eggert, Physik. Zeitschr. 20, 570 (1919).

The first equation represents the primary ionization stage, and the second, the secondary stage. The two groups of curves, Figure 119, represent the degree of ionization as a function of temperature and pressure. It is evident that no line of the normal atom can be present under ordinary pressure of one atmosphere at a temperature of 12,000° C., since the normal atoms are all ionized under these conditions; it is equally obvious that the spectral lines peculiar to the ionized atom must make their appearance until they, too, will vanish when the temperature has been raised to 20,000°, the pressure being kept constant at one atmosphere. Arc and spark spectra of calcium are well known spectroscopically. The line $\lambda = 4{,}227$ Å. is characteristic of the former, while the lines H and K (wave-lengths 3,968, 3,934), recognized as prominent Fraunhofer lines, are characteristic of the latter.

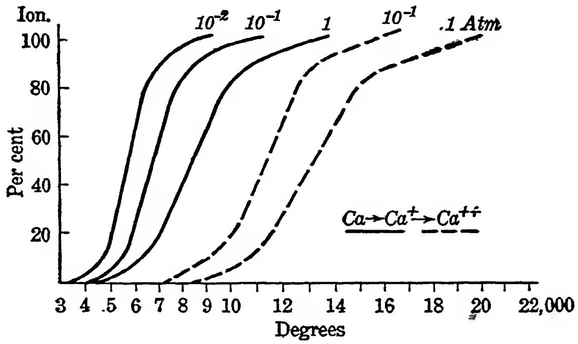

FIG. 119.

The appended tabular summary (see next page) indicates the classes of stars (spectral classes) that contain these lines. The table likewise shows similar data for the hydrogen lines and for the lines of normal and of ionized helium. The lines of doubly ionized calcium, unfortunately, are not yet known.

The last column of the table lists the temperature estimated by means of the previous considerations; in other words, it is a spectroscopic temperature determination which agrees fairly well with the value calculated from the radiation theory, listed in the second column.

Spectral Class	Light	Temperature, Determined from the Energy Distribution in the Spectrum	Hydrogen Spectrum	Calcium Normal Atom	Calcium Ion Ca⁺	Helium Atom	Helium Ion	Spectral Temperature
P........	Fog, with few bright spectral lines	> 23,000°	No atom-lines ↓			Weak or no lines	He⁺ maximum intensity	24,000° 22,000°
O........	White	20,000°			Ca⁺-lines weak ↓	Maximum intensity		18,000°
B........	Violet, very strong	14,000°						14,000°
A........		11,000° 9,000°	Balmer-series maximum ↑	Atom-lines weak ↓				12,000°
F.......	Yellow	7,500°						
G.......	(Sun)	7,000° 6,000° 4,500°		Increasing intensity ↑	Maximum intensity ↑			9,000°
K........			Balmer-series weak					7,000°
M........	Red (sun-spots)	3,000°		Maximum intensity of Ca-lines	No Ca⁺ lines			5,000° 4,000°

It does not matter very much if complete agreement has not yet been obtained in all these data; pressure estimates at best are very uncertain and furthermore the pressure itself is not constant throughout the entire layer.

In conclusion we will cite a classic example for the application of Saha's theory. Whereas the sodium D-lines are extremely prominent in the solar spectrum, they are absent completely in the spectrum of the chromosphere. Should the presence of sodium be questioned because of this apparent discrepancy in results? By no means! The pressure within the chromosphere is so low and its temperature of such value that all sodium atoms are ionized. Obviously, therefore, the D-lines, as characteristic lines of the normal atom, cannot be present, and, furthermore, the lines of Na^+ cannot be observed, because they are situated beyond the ultra-violet boundary imposed on observation by the absorption in the atmosphere. In sun-spots, on the other hand, the temperature is lower and the D-lines make their appearance with maximum intensity. Here the ionization of the atom is entirely repressed.

We thus conclude our considerations of this subject. Atomic physics has invaded and conquered a new field and has demonstrated its utility as a mode of investigation. But we may add that we are only at the beginning of newer developments.

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